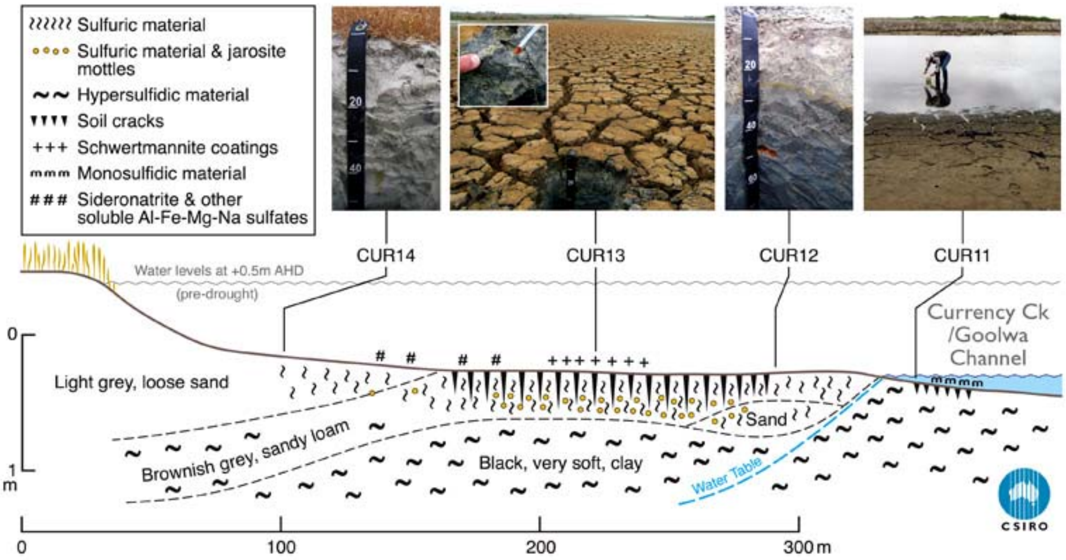

Acid Sulfate Soil Assessment in Finniss River, Currency Creek, Black Swamp and Goolwa Channel, South Australia

R.W. Fitzpatrick, G. Grealish, P. Shand, S.L. Simpson, R.H. Merry and M.D. Raven

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Prepared for

Murray-Darling Basin Authority (MDBA)

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Conceptual soil toposequence model constructed from field site transect and laboratory analyses data that characterises the spatial variation of the various types of materials in acid sulfate soils. The toposequence figure describes the cross-section from the Goolwa Channel/Currency Creek waters to elevated land. Prominent brownish-orange coatings of the mineral schwertmannite occurs on the soil surface, which is a good mineral indicator of the presence of sulfuric material (pH <4), that has formed in the upper layers and below this is hypersulfidic material. With the receding water levels due to current extreme drought conditions the previously hypersulfidic subaqueous soils have been exposed, dried and reacted with oxygen from the air to form sulfuric soils that have cracks and columnar structure.

Figure constructed by Gerard Grealish and Rob Fitzpatrick, drawn by Gregory Rinder ©2009 CSIRO

ACKNOWLEDGEMENTS

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We would like to acknowledge the efforts of CSIRO staff: B.P. Thomas and N.L. Creeper who assisted with field work; N. Jayalath who conducted the pH testing; J. Charlesworth and I. Hamilton for undertaking the metal mobilisation tests; L. Bardwell and C. Jarolimek for analysing the metals samples. Warren Hicks and Mark Thomas for providing review comments and edits on the report.

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EXECUTIVE SUMMARY

Background and Aim

This report provides data and assessment of the properties, extent and presence (or absence) of various subtypes of acid sulfate soils (ASS) in the lower reaches of Finniss River, Currency Creek, Black Swamp and Goolwa Channel regions in South Australia. This report provides consolidated and additional data to the preliminary report published in January 2009 (Fitzpatrick *et al.* 2009a). These areas (Figure 1-1), adjacent to Lake Alexandrina in the lower reaches of the River Murray in South Australia, have recently experienced falling and historically low water levels due to extreme drought conditions. The exposure and drying of hypersulfidic materials can potentially have serious environmental consequences relating to soil and water acidification, metal mobilisation, de-oxygenation of water, or formation of malodours (H_2S, organo-S compounds).

This study aimed to verify the presence (or absence) of acid sulfate soils in the Finniss River, Currency Creek, Goolwa Channel and Black Swamp/Tookayerta Creek areas that are adjacent to Lake Alexandrina, assess the hazards of any acid sulfate soil material found, and to determine the surface water quality of waters present in the area.

Key Finding

More than half of the sites investigated contained sulfuric material (pH < 4.0). The remainder of sites have significant potential for further developing sulfuric materials from hypersulfidic materials if the water levels continue to drop, although the risk of this occurring is low to moderate provided the materials are kept under anaerobic conditions.

The additional field and laboratory data confirmed previous predictions (Fitzpatrick *et al.* 2008b; 2009) that large areas of extremely acidic soils (sulfuric materials: pH < 4.0) are present, i.e. approximately 2000 ha of sulfuric soils occur at a water level of -1.0m Australian Height Datum in this study area.

Fitzpatrick et al. (2009a) recommended that monitoring be considered an essential component of acid sulfate soil risk assessments during the current drought, and emphasised that it will be particularly important during rewetting phases in sulfuric soils from winter rainfall events when acidity and metal mobilisation may occur. A significant new finding in May 2009 is the identification of acidic (pH 3.8 to 3.3) ponded and flowing water bodies in localised areas previously identified as containing widespread sulfuric cracking clay soils.

Extent of Data Collection

In this study, 12 transects that included 39 geographically well-distributed and locally representative soil profiles were investigated. A total of 143 layers were described, that included 119 soil samples and 17 water samples for laboratory analysis, and 9 layers of surface salt efflorescences.

Conceptual Toposequence Models

Areas were characterised by placing sites along toposequence-based transects from dry inland areas down to water level. This allowed the layer distribution of materials to be better understood and very detailed conceptual toposequence models have been constructed to provide an improved understanding of the temporal and spatial extent of the acid sulfate soil materials (Figure 4-1, Figure 4-2, Figure 5-1, Figure 6-1, Figure 6-2, Figure 6-3). These figures show that sulfuric material occurs not only on the dry soil surfaces but also down to 30 cm depth in both dry and rewetted soils, and that the strongly acidic layers are common in both sandy and clayey soils that have cracked to form columns. Hypersulfidic material occurs either below the sulfuric layer or below surface water bodies (subaqueous) or the water table in the soil. The hypersulfidic layer ranges in thickness up to, and in some areas more than one metre, and it is often formed in black, soft clay.

The conceptual toposequence models provide an understanding of the soil distribution that then allowed the earlier predictive maps to be tested and updated with more confidence. Large areas of extremely acidic soils (sulfuric materials: pH < 4.0) were present and confirmed previous predictions (Fitzpatrick et al. 2008b) that these areas have a high potential of developing sulfuric materials (i.e. soil pH < 4). There is also a high potential of developing more sulfuric materials from existing hypersulfidic materials, which have not yet oxidised. These maps are presented in Figure 9-1.

Acid Generating Potential

The combined standard methodologies described in this report using: (i) soil morphology, (ii) field pH testing, (iii) pH peroxide testing, (iv) acid-base accounting, (v) soil incubation (ageing) and (v) mineralogical analyses has confirmed these soils either contain sulfuric acid (sulfuric material, pH ≤ 4), or have the potential to oxidise and form sulfuric acid when exposed to air (oxygen) because of high concentrations of sulfide minerals (hypersulfidic material). The occurrence of both sulfuric and sulfidic materials is believed to be causing acidic soil and waters within the study area.

The highest risk of acidification is clearly related to the soils and sediments which already contain sulfuric material; these materials occur in more than half of the sites investigated.

For the remainder of sites there is significant potential for acidification of soils with sulfidic materials but the risk of this occurring is low to moderate provided they are kept under anaerobic conditions.

Metals and Mobilisation

Metal mobilisation is likely to be most significant in sulfide-containing soils that have undergone oxidation. Sulfide minerals scavenge trace metals, and if so, may release the metals during oxidation.

During 24 h mobilisation tests, the water pH generally became similar to that measured for the soils. The release of nitrate and phosphate from the dried soils was low. The metal release was rapid and dissolved concentrations of Al, Cd, Co, Cu, Cr, Mn, Ni, V and Zn greatly exceeded the Australian water quality guidelines (WQGs) for protection of ecosystem health. For Al, Cd, Co, Cu, Cr, Ni and Zn, the concentrations were often greater than 100×WQGs and Al and Co frequently exceeded 1000×WQG values.

Greater concentrations of metals were released from Finniss River soils than from Currency Creek soils. In general, the concentrations of metals released increased greatly at pH < 5.

The tests demonstrated that the rewetting of dried acid-sulfate soils has the potential to release significant quantities of environmentally degrading substances.

Although not investigated, the attenuation of dissolved metal concentrations through co-precipitation and adsorption to aluminium and iron oxyhydroxide phases is likely to occur as acidic, metal-rich waters mix with more neutral or alkaline water.

Mineralogy

At several sites, abundant occurrences of acidity indicating minerals were observed in salt efflorescences and sub-surface horizons. Bright yellowish green and orange surface efflorescences and pale yellow mottles in subsoils were present and X-ray diffraction analyses showed that these were sideronatrite, schwertmannite and jarosite/natrojarosite minerals, respectively. The pH values of the bright yellowish green surface efflorescences are very acidic (pH < 2) and the orange and pale yellow minerals are acidic (pH < 3 to 4).

The presence of all of these minerals indicates high contents of iron sulfides (principally pyrite) in the original materials. It is predicted that large quantities of sulfuric acid will be produced in the hypersulfidic, subaqueous soils if the river levels continue to drop significantly and the adjacent wet soils are allowed to dry. Where winter rainfall has re-wet previously identified sandy sulfuric soils with pH values of 1.6 to 2.5, we found tamarugite [$NaAl(SO_4)_2.6H_2O$], with traces of sideronatrite and pH values ranging from 0.5 to 0.8.

Hydrogeochemistry

Some of the waters in soil pits of the dry river-beds and wetlands of Currency Creek (with deep cracks) and Finniss River (sands) had low pH values ranging from 3.4 to 3.9. Some river waters sampled in Currency Creek and Black Swamp in November 2008 contain moderate to low concentrations of alkalinity (<117 mg/L and 31 mg/L respectively as HCO_3).

Acid sulfate soil influences on the low alkalinity in Currency Creek are likely when compared to the high alkalinity of Lake Alexandrina water (currently in the range 200 to 250 mg/L). The alkalinity of Lake Alexandrina helps to maintain the alkalinity of the remnant Currency Creek and Finniss River waters, along with local contributions from ground waters and evapo-concentration.

The data from Wally’s Landing (Finniss River) in May 2009 showed that the pH in the flowing river was circum-neutral following re-wetting from recent winter rainfall. Water in cattle pugs close to the river was found to be very acidic (pH 3.2). In an adjacent tributary we identified acidic (pH 3.3. to 4) flowing stream water with relatively high specific electrical conductance (SEC) of 13300 $\mu S\ cm^{-1}$).

Hazard assessment

Hazard assessment is based on a framework used for coastal acid sulfate soil assessment, as discussed in the report, it provides a means to compare soils relatively and identify those of concern. Based on this assessment framework 37 of the 39 sites (94%) have sufficient net acidity that, if disturbed, would be a site of concern. More than 91% of the sites assessed have a high, very high, or extra high hazard classification indicating a significant potential acid hazard.

Predictive acid sulfate soil chronosequence model

A predictive acid sulfate soil chronosequence model illustrating the formation and transformation of sulfidic materials has been constructed for the Finniss River using Wally's Landing and adjacent wetlands as a case study. This provides an understanding of how these soil materials change with time and the events involved to make this happen.

Based on field investigations and historical/palaeo-pedological knowledge of the Finniss River, a series of nine conceptual models have been constructed that illustrate how various acid sulfate soil materials have sequentially changed under subaqueous, waterlogged (saturated) and dried conditions, and have further changed, because of recent re-wetting by winter rainfall events.

Recommendations

Monitoring is considered an essential component of acid sulfate soil assessments, not only during the current drought, but also during the re-wetting phases when acidity and metal mobilisation are likely to occur. It is recommended that monitoring be completed as follows:

(i) Temporal monitoring to be completed at several selected "reference sites" every two to three months, or in relation to change in 'wetness' condition, to determine future changes in acid generation.

(ii) Spatial monitoring on a monthly basis (or when there is a rapid water level change) at the sites sampled in this study, to assess spatial trends.

(iii) Undertake a detailed acid sulfate soil survey and investigation of the wetland area north of Wally's Landing, that is a source of the acidic surface water, to quantify the source, extent and storage of acid.

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1. INTRODUCTION

This report provides data and assessment of the properties, extent and presence (or absence) of various subtypes of acid sulfate soils (ASS) in the lower reaches of Finniss River, Currency Creek, Black Swamp and Goolwa Channel regions. It provides consolidated and additional data to the preliminary report published in January 2009 (Fitzpatrick *et al.* 2009a). These areas (Figure 1-1), adjacent to Lake Alexandrina in the lower reaches of the River Murray in South Australia, have recently experienced falling and historically low water levels due to drought conditions. The exposure and drying of hypersulfidic materials can potentially have serious environmental consequences relating to soil and water acidification, metal mobilisation, de-oxygenation of water, or formation of malodours (SO_2, H_2S, organo-S compounds). This report consolidates and presents results and conclusions from:

(i) a nine-day program of field work conducted from 18th to 26th November 2008,

(ii) laboratory data analysis of soil and water samples collected throughout the area,

(iii) data from several return field trips between December 2008 and May 2009, and

(iv) data collected from the initial Rapid Assessment Survey in July 2008.

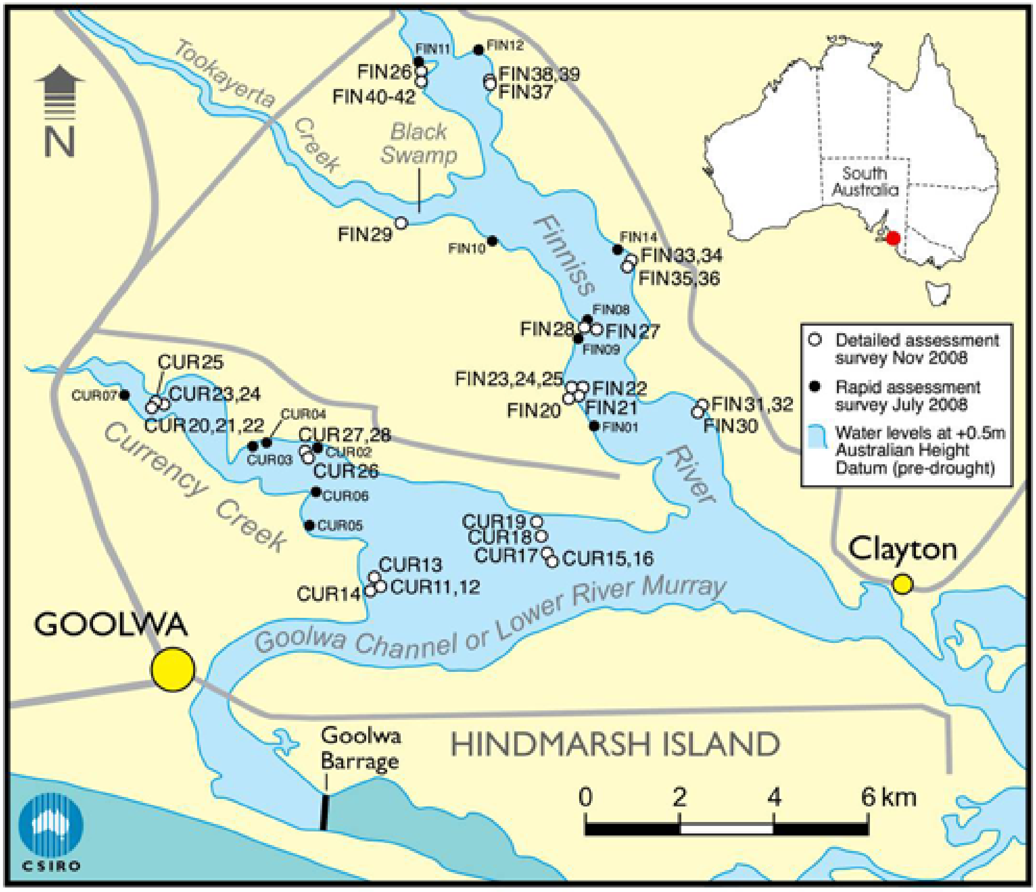


Figure 1-1: Map showing survey area and location of all detailed assessment survey sites for Finniss River (FIN 20 to 28, 30 to 42), Currency Creek (CUR 02 to 07, 20 to 28), Goolwa Channel (CUR 11 to 19) and Black Swamp (FIN29). The map also shows the location of the earlier rapid assessment survey sites.

1.1. Aims and Objectives

The aims of this investigation are to:

(i) Verify and update the properties, extent and presence (or absence) of the types of acid sulfate soil materials in Finniss River, Currency Creek, Black Swamp and Goolwa Channel region, South Australia.

(ii) Identify the acid sulfate soil material characteristics to assist others with determining potential management options to minimise the impact of acid sulfate soil materials to the environment and to recommend future monitoring options.

To achieve these aims, the following detailed objectives were identified:

- Conduct field investigations to assist with determining extent, and then to link surface observable features with underlying hidden materials.
- Provide soil descriptive information for select sampling sites that are representative of the region and potential locations for acid sulfate soil materials.
- Collect soil and water samples for laboratory analysis and in chip-trays.
- Conduct laboratory analysis that includes pH, acid-base accounting, and metal release experiments according to methodologies agreed for the Murray-Darling Basin Authority (Fitzpatrick *et al*. 2009b).
- Assess acidification potential using peroxide testing, pH changes with incubation, and acid-base accounting,
- Conduct X-ray diffraction analyses on a representative range of hand-picked samples to determine the dominant mineralogical composition of key acid sulfate soil features (e.g. acidic bright yellowish and reddish-orange coloured salt efflorescences, coatings and mottles) observed in the field.
- Compile a database that includes soil descriptive information, soil analytical data, photographs of the soil and landscape, and spatial information plotted against existing imagery.
- Interpret the available information to determine the acid sulfate soil hazard for the site locations.
- Construct conceptual models to describe the soil material variation based on the information from field transect site data and laboratory investigations. Discuss the possible factors contributing to previous, current and future acid sulfate soil formation in these landscapes.
- Provide verbal briefings and short summary reports to Murray-Darling Basin Authority and Department of Environment and Heritage (South Australia) based on field work, pre-laboratory testing (pH and peroxide tests), and laboratory results as completed.
- Prepare a preliminary report on initial field observations from the November 2008 field work to provide early information on findings, published in January 2009 (Fitzpatrick *et al.* 2009a)

- Prepare a report (this report) consolidating all data and discussing the findings and conclusions on the properties, extent and potential severity of acid sulfate soil materials, including monitoring recommendations.

1.2. Background

Acid sulfate soils are those soils containing iron sulfide minerals (e.g. Pons 1973; Fanning 2002). These soils may either contain sulfuric acid (sulfuric material), or have the potential to form sulfuric acid (sulfidic material), or cause de-oxygenation (monosulfidic material), or release contaminants when the sulfide minerals are exposed to air (oxygen). Acid sulfate soils form naturally when sulfate in the water is converted to sulfide by bacteria. These sulfides react with metals, especially iron (Fe), to form sulfidic materials (typically pyrite: FeS_2) in subaqueous acid sulfate soil or sediments in rivers and wetlands.

Changes to the hydrology in regulated sections of the Murray-Darling Basin (MDB) system, and the chemistry of rivers and wetlands have caused significant accumulation of sulfidic material in sub-aqueous and margin soils. If left undisturbed and covered with water, sulfidic material poses little or no threat. However, when sulfidic material is exposed to the air, the sulfides react with oxygen to form sulfuric acid (i.e. sulfuric materials with pH < 4). When these sulfuric materials are subsequently covered with water, significant amounts of sulfuric acid can be released into the water.

Other risks associated with acid sulfate soils include: (i) mobilisation of metals, metalloids and non-metals, (ii) decrease in oxygen in the water column when monosulfidic materials are mobilised into the water column, and (iii) production of noxious gases. In severe cases, these risks can potentially lead to damage to the environment, and have impacts on water supplies, and human and livestock health.

As water levels decline in Lake Albert and Lake Alexandrina (the Lower Lakes) and the River Murray system below Blanchetown (Lock 1), due to the current, unprecedented drought conditions, the anaerobic sulfidic materials that were once covered by water are now exposed to oxygen at the river and lake margins, and in adjacent wetlands. With continued lowering of water levels, the hypersulfidic material can become progressively oxidised to greater depths of the soil profile, generating sulfuric material (pH < 4).

Despite decades of scientific investigation of the ecological (e.g. Living Murray Icon Site Environmental Management Plan: MDBC, 2006a,b,c), hydrological (salinity), water quality and geological features of wetlands in the Murray-Darling Basin, we have only recently begun to appreciate the wide spectrum of acid sulfate soil subtypes and processes that are operating in these contemporary environmental settings - especially from continued lowering of water levels (e.g. Fitzpatrick *et al.* 2008a,b,d,e; 2009a; Lamontagne *et al.* 2004; Shand *et al.* 2008a,b; Simpson *et al.* 2008). Hence, the Murray-Darling Basin Ministerial Council at its meeting in March 2008 directed the then Murray-Darling Basin Commission (MDBC) to undertake an assessment of acid sulfate soil risk at key wetlands in the Murray-Darling Basin. The Murray-Darling Basin Commission (now the Murray-Darling Basin Authority), in partnership with its Partner Governments and scientists, designed the Murray-Darling Basin ASS Risk Assessment Project, which aims to assess the spatial extent of, and risks posed by acid sulfate soils in the Murray-Darling Basin. The project also aims to identify and assess broad management options.

The project established a list of more than 10,000 wetlands that were then assessed against a number of criteria aimed at identifying those that had potential for acid sulfate soil occurrence. Due to their ecological significance, the decision was made to initially target Ramsar-listed wetland complexes of the Murray-Darling Basin (e.g. including

South Australia's Lower Lakes region). Wetlands within these complexes were identified for further rapid or detailed assessment. Because this area was likely to contain acid sulfate soil, a rapid assessment was conducted using the Murray-Darling Basin Authority's 'Acid Sulfate Soils Field Guide', this comprised field measurements of water quality and wetland sediments. The data collected through this rapid assessment (see data in Appendix 1 and locations shown in Figure 1-1) were screened by CSIRO using agreed criteria. CSIRO identified this area as having an increased likelihood of developing significant amounts of sulfuric materials and recommended to Murray-Darling Basin Authority and Department of Environment and Heritage (South Australia) that it required further investigation under the detailed assessment methodology. These standardised methods are currently being documented in a sampling and analysis protocol for the Murray-Darling Basin Authority (Fitzpatrick *et al.* 2009b).

1.3. Summary of Previous Work

Previous studies by CSIRO Land and Water developed a conceptual model (Figure 1-2) to describe four sequential drying phases and the development of different acid sulfate soil subtypes (Fitzpatrick *et al*. 2008b) that occur. Applying this model, Fitzpatrick *et al*. (2008b,c) integrated locally detailed field survey and laboratory data and used the Australian Soil Classification (Isbell 1996) to derive fourteen subtypes of acid sulfate soil conforming to the map legend of the Atlas of Australian ASS (Appendix 2).

A series of conceptual process models for each of the lakes (Alexandrina and Albert) and lower River Murray systems were applied to:

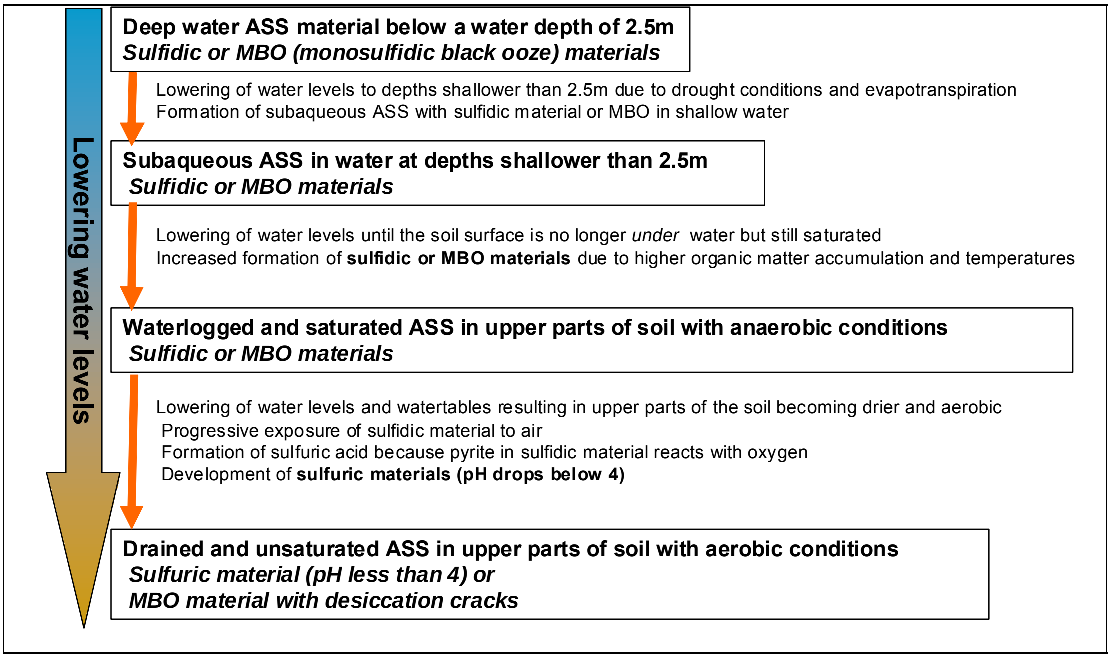
- explain the sequential formation and transformation of sulfidic material to sulfuric material in various subtypes of acid sulfate soil (5,500 B.C.E to the extreme drought conditions of 2006-2008),
- explain and predict new occurrences of minerals, their formation and transformation (e.g. pyrite to sideronatrite; sideronatrite to schwertmannite; pyrite to natrojarosite), and
- predict the impacts of further drought on acid sulfate soil oxidation and impacts.

Combined bathymetry, soil and vegetation mapping in a geographic information system (GIS) framework was used to help predict the distribution of different subtypes of acid sulfate soil according to three predictive scenario maps (Fitzpatrick *et al*. 2008a,b), which in Figure 1-3 depict sequential changes in acid sulfate soil materials at different water levels in Lake Alexandrina and tributaries (e.g. Finniss River).

These predictive acid sulfate soil maps are constantly being revised as new information becomes available through site visits, field testing and the availability of new spatial data sets (e.g. Fitzpatrick *et al*. 2008b; p. 59; 2009a).

High sulfide contents were previously measured in a subaqueous sulfidic soil in the Finniss River at site AA26 adjacent to FIN26 (Figure 1-1), which also had relatively low acid neutralising capacity in the upper soil layers (i.e., low carbonate concentrations (Fitzpatrick *et al*. 2008b; p. 118; 2009a).

Field studies combined with the maps and predictive models were used to conclude that most of this region could produce sulfuric material if the water level fell to –1.5 m AHD (see predictive scenario shown in the acid sulfate soil maps in Figure 1-2 and Figure 1-3; and graphically in Figure 1-4.



Deep water ASS material below a water depth of 2.5m
Sulfidic or MBO (monosulfidic black ooze) materials

Lowering of water levels to depths shallower than 2.5m due to drought conditions and evapotranspiration
Formation of subaqueous ASS with sulfidic material or MBO in shallow water

Subaqueous ASS in water at depths shallower than 2.5m
Sulfidic or MBO materials

Lowering of water levels until the soil surface is no longer *under* water but still saturated
Increased formation of **sulfidic or MBO materials** due to higher organic matter accumulation and temperatures

Waterlogged and saturated ASS in upper parts of soil with anaerobic conditions
Sulfidic or MBO materials

Lowering of water levels and watertables resulting in upper parts of the soil becoming drier and aerobic
Progressive exposure of sulfidic material to air
Formation of sulfuric acid because pyrite in sulfidic material reacts with oxygen
Development of **sulfuric materials (pH drops below 4)**

Drained and unsaturated ASS in upper parts of soil with aerobic conditions
Sulfuric material (pH less than 4) or
MBO material with desiccation cracks

Figure 1-2: Generalised conceptual model showing the sequential transformation of four Classes of acid sulfate soil due to lowering of water levels (from Fitzpatrick *et al*. 2008a, b, c, d).

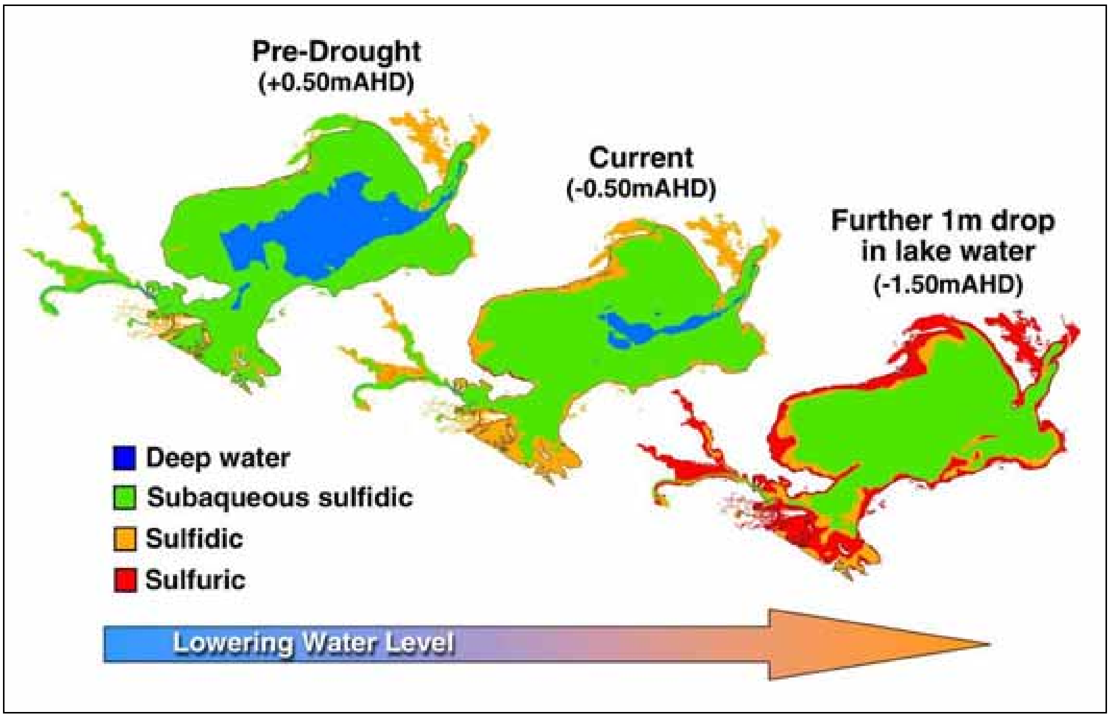


Figure 1-3: Predictive scenario maps depicting changes in acid sulfate soil materials at different water levels in Lake Alexandrina (+0.5 m AHD, –0.5 m AHD and –1.5 m AHD) from Fitzpatrick *et al*. 2008b. Finniss River, Currency Creek and Goolwa Channel are the three extensions occurring on the left side of Lake Alexandrina.

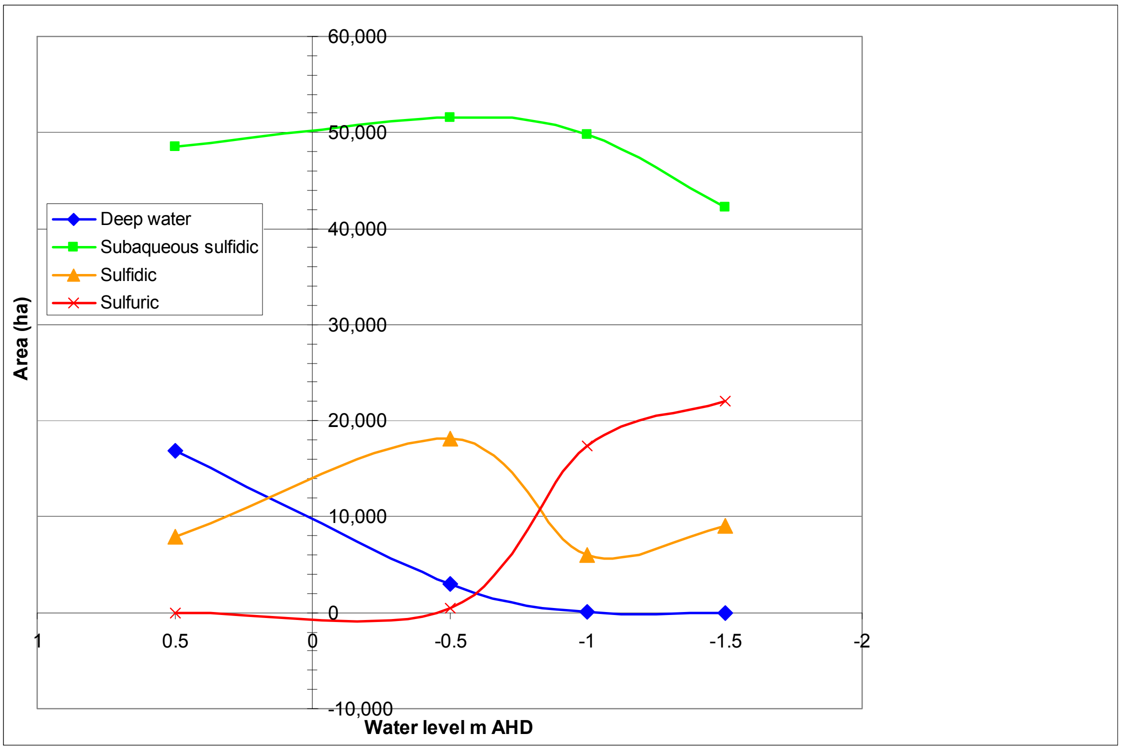


Figure 1-4: Graphic depiction of modelled changes in acid sulfate soil material aerial extents at different water levels in Lake Alexandrina (+0.5 m AHD, –0.5 m AHD and –1.5 m AHD).

1.4. Classification of Acid Sulfate Soil Material

Recently, the Acid Sulfate Soils Working Group of the International Union of Soil Sciences agreed to adopt in principle the following five descriptive terminology and classification definitions of acid sulfate soil materials proposed by Sullivan *et al*. (2008) at the 6th International Acid Sulfate Soil and Acid Rock Drainage Conference in September 2008 in Guangzhou, China. This new classification system for acid sulfate soil materials has also been recently (October 2008) adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Group for use in the detailed assessment of acid sulfate soils in the Murray-Darling Basin.

The criteria to define the soil materials are as follows:

Acid Sulfate Soil Materials

1. **Sulfuric materials** – soil materials currently defined as sulfuric by the Australian Soil Classification (Isbell 1996). Essentially, these are soil materials with a $pH_w < 4$ as a result of sulfide oxidation.

2. **Sulfidic materials*** – soil materials containing detectable sulfide minerals (defined as containing greater than or equal to 0.01% sulfidic S). The intent is for this term is to be used in a descriptive context (e.g. sulfidic soil material or sulfidic sediment) and to align with general definitions applied by other scientific disciplines such as geology and ecology (e.g. sulfidic sediment). The method with the lowest detection limit is the Cr-reducible sulfide method, which currently has a detection limit of 0.01%; other methods (e.g. X-ray diffraction, visual identification, Raman spectroscopy or infra red spectroscopy) can also be used to identify sulfidic materials.

   **This term differs from previously published definitions in various soil classifications (e.g. Isbell, 1996).*

3. **Hypersulfidic material** - Hypersulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by having a field pH of 4 or more and by experiencing a drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2-10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is either:
    a. until the soil pH changes by at least 0.5 pH unit to below 4, or
    b. until a stable pH is reached after at least 8 weeks of incubation.
4. **Hyposulfidic material** - Hyposulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by having a field pH of 4 or more and by not experiencing a drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2-10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is until a stable pH is reached after at least 8 weeks of incubation.
5. **Monosulfidic materials -** soil materials with an acid volatile sulfur content of 0.01%S or more.

2. FIELD AND LABORATORY METHODS

Following a request from the Murray-Darling Basin Authority, CSIRO Land and Water were engaged to conduct a Phase 1 detailed assessment with some selected Phase 2 analyses (that included incubation of samples in chip trays, rapid metal release, XRD and XRF analyses) of acid sulfate soil at the in the lower reaches of Finniss River, Currency Creek, Black Swamp and Goolwa Channel areas.

2.1. Detailed Acid Sulfate Soil Assessments Using Two Phases

In summary the protocol being developed by the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project Scientific Reference Panel (Fitzpatrick et al. 2009b) requires a two-phase procedure.

Phase 1 aims to determine whether or not acid sulfate soil materials are likely to be present by:

a) Consulting with relevant managers of that wetland.
b) Photographic record of sites and soil profiles.
c) Field descriptions of soils and sampling, including pH (e.g. using Merck pH indicator strips) and specific electrical conductance (SEC) testing.
d) Sampling and sub-sampling of soil in chip-trays.
e) Field testing of water quality parameters (pH, specific electrical conductance (SEC), redox potential (Eh), dissolved oxygen (DO), alkalinity by titration, and turbidity.
f) Laboratory analysis to conclusively identify the presence or absence of sulfuric, sulfidic or monosulfidic materials using incubation (ageing pH) in chip-trays, pH peroxide testing (pH_{FOX}), sulfur suite and acid base accounting: S_{CR} (sulfide % S), pH_{KCl}, and TAA (titratable actual acidity: moles H^+/tonne); acid neutralising capacity (ANC) where soil materials were sulfidic, and water-extractable SO_4 (1:5 soil:water suspension),
g) Surface water and groundwater chemical and nutrient analyses.

Phase 2 investigation will be recommended only if acid sulfate soil materials (e.g. sulfuric, hypersulfidic or hyposulfidic or monosulfidic materials or surface materials with high water soluble sulfate contents (i.e. potentially monosulfidic materials) or other acidic soil materials have been detected in soil profiles, and will be conducted (on the soil material collected during Phase 1) to determine the nature and severity of the environmental risks posed by acid sulfate soil materials. The Phase 2 analyses comprise:

a) Continued incubation of samples in chip-trays.
b) More detailed acid/base accounting (e.g. elemental sulfur and acid volatile sulfur).
c) Rapid metal release.
d) Contaminant and metalloid dynamics.
e) Monosulfide formation potential.
f) Mineralogy by X-ray diffraction (XRD).
g) Major and trace elements by X-ray fluorescence spectroscopy (XRF).
h) Archiving of all soil samples in CSIRO archive (as chip-trays and bulk samples).

Note that this report details all Phase 1 investigations and selected Phase 2 investigations that include continued incubation, rapid metal release, and mineralogy.

2.1.1. Ranking criteria for soil materials for detailed assessment

It was recommended that soil materials be assigned the following priorities to undertake detailed Phase 2 investigations:

High Priority

1. All sulfuric materials.
2. All hypersulfidic materials as recognised by either (1) incubation of sulfidic materials or (2) a positive net acidity result with a Fineness Factor of 1.5 being used.
3. All hyposulfidic materials with S_{CR} contents ≥ 0.10%S.
4. All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents >100 mg SO_4/L.
5. All monosulfidic materials.

Moderate Priority

1. All hyposulfidic materials with S_{CR} contents < 0.10% S.

No further assessment

1. Other acidic soil materials.
2. All other soil materials.

2.2. Field Sampling of Soil

Field survey work was conducted between 18th and 26th November 2008. During this time 39 sites were visited and 143 soil layers described and sampled. The guiding principles for selection of the sites included that they were to be regionally representative and of a sufficient geographic spread for the study area. They also covered the landscape positions (river channels, wetlands, lowlands, and shorelines) and the different types of soils (sub-aqueous, waterlogged and drained soil profiles), and assessed current and potential impacts of acid sulfate soils during the current extreme drought conditions. The distribution of these site locations is shown in Figure 1-1. These sites were also easily accessible at the time the study was undertaken. As such, these sites could form the basis for any future monitoring program.

The approach was to place sites to form a transect, with sites chosen to cover the range of soils from the water to the step-up high edge where reeds were growing. The sample site location and number of sites placed was determined by the experience of the field soil surveyor. A number of factors were taken into consideration, including but not limited to the following: safe access and working area, ease of access (farm tracks, gates, proximity to public roads and permission from landholders), visually observed variability (vegetation habitat changes, soil surface condition changes, water on the surface, topography changes), observed variability on the image maps, and information about the area supplied by the knowledge of landholders and Natural Resource Management staff and the data from the earlier Rapid Assessment Survey in July 2008 (Appendix 1).

Sample site location coordinates were obtained using a global positioning system (GPS), using the WGS 84 Datum: Zone 54 South. At dry sites soil samples were taken from soil pits dug to approximately 0.6 m deep, and then with a gouge auger below the base of the pit down to 1.6 m or to auger refusal. Where soils were below water (i.e. subaqueous soils), samples were obtained by wading and using a shovel to grab the upper 10 to 20 cm and then a gouge auger, to approximately 1.6 m depth or to auger refusal. Irrespective of the sampling method to extract soil material, soil profiles were sampled on a layer-by-layer basis where changes (colour, morphology) in the soil material were identified. About 4 to 6 layers were sampled per soil profile and generally the layers consisted of a surface (about 0 to 5 centimetres), subsurface (5 to 20 centimetres), subsoil (about 20 to 50 centimetres), deep subsoil (50 to 100 centimetres), subdivisions of the above intervals and a deeper layer below, if extracted.

The samples were described according to standard methodology (McDonald *et al*. 1990; Schoeneberger *et al.* 2002). Layer depth ranges were recorded and for each layer the morphology and physical properties described included: colour (matrix and mottles), texture, structure, consistency, and occasional other identifiable features such as stickiness, plant material, odour and concentrations.

Multiple soil samples were taken from each layer and included:

- Bulk soil samples (typically > 500 g) were placed in pre-labelled, thick, sealable plastic bags and mixed up, for peroxide pH analysis and bulk storage.
- Two sets of sub-samples from the bag were taken and placed in two 70 ml screw-top plastic jars, with care taken to exclude air by filling the jars to the maximum level to limit sulfur oxidation during transit and storage. One for XRD (powder X-ray diffraction) and XRF (X-ray fluorescence spectrometry) analyses, and the other for chromium reducible sulfur (S_{CR}) analyses.
- Two sub-samples from the layers were placed in two separate chip-trays, one used to display morphologically representative aggregates for each of the sampled layers for later visual reference (e.g. during report writing and placed in the CSIRO Land and Water soil archive), and the second chip-tray was used for acid sulfate soil incubation (pH ageing) in the laboratory.

Occasionally, samples of acidic yellowish and reddish-orange coloured salt efflorescences, coatings and mottles were described and carefully collected for mineralogical analyses using XRD.

Physical limitations to sampling caused by the soil materials, for example unconsolidated coarse (sandy layers), or extremely hard dry layers or deep water occasionally made recovery of profile samples difficult in some places. However, the samples obtained during this study from these situations were adequate to characterise materials.

2.3. Field Sampling of Water

For sites where surface water, water between surface cracks or water at the base of a pit occurred water measurements were made and water samples collected.

Water samples were collected for chemical analyses at several sites. Dissolved oxygen (DO), pH, and redox potential (Eh) were measured on-site using a calibrated YSI multi-parameter meter and electrodes. Other on-site measurements included temperature (T ^{o}C), specific electrical conductance (SEC or EC) and alkalinity (by titration). Samples were collected for major and trace chemical analyses in 125 ml polyethylene bottles. Those for major and trace element analysis were filtered through 0.45 µm membrane filters and the aliquot for cation and trace elements were acidified to ca. 0.2 % v/v HCl to minimise adsorption onto container walls.

2.4. Laboratory Analysis

The general flowchart for soil sample collection and analysis is shown in Figure 2-1. Air was excluded as far as possible from the samples. On return to the laboratory the soils were kept cool at 4°C until analysed. Samples (soils and salts) for XRF and detailed sulfide analysis (S_{CR}) for acid-base accounting were air dried at 80°C. Moisture contents were recorded and bulk densities estimated. Samples for sulfide analysis were sent to the Environmental Analysis Laboratory at Southern Cross University. Recorded locations and long-term storage of the oven dried samples and air dried/moist samples kept in chip trays allow for future re-sampling and analysis, if required.

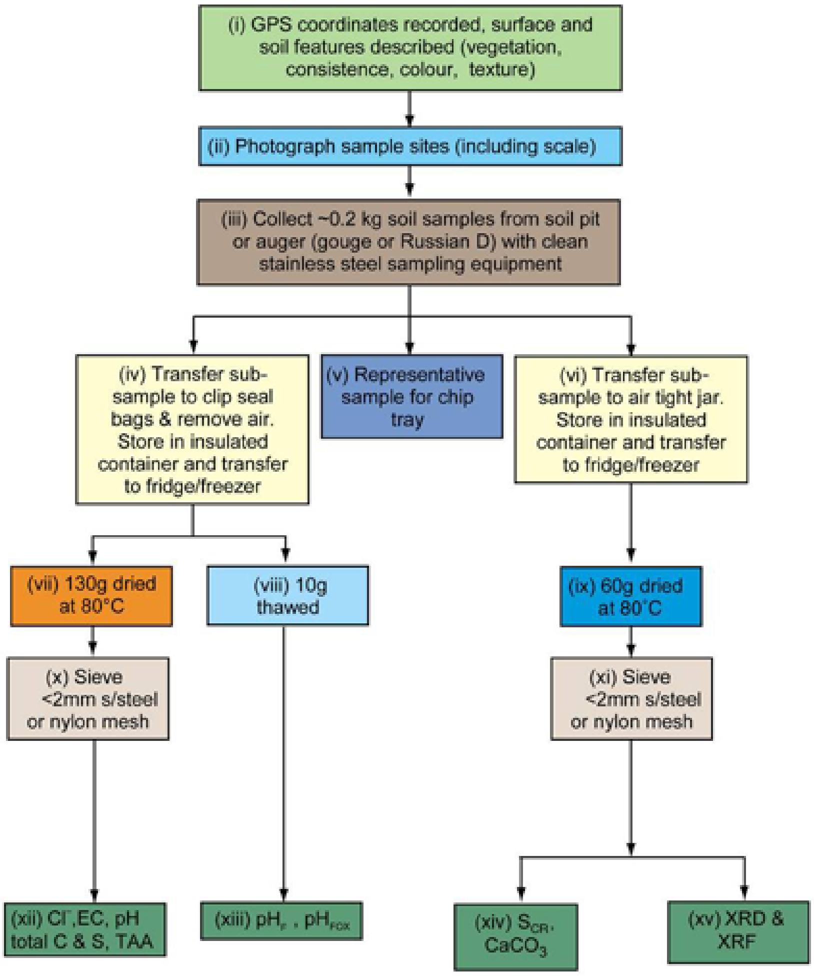


Figure 2-1: General flow chart for soil sampling and analysis.

2.4.1. Methodologies used to assess acid generation potential

In order to assess the acid generation potential (AGP) of acid sulfate soils, a range of methodologies are used. This requires several parameters to be measured, as highlighted on Figure 2-1. An important consideration also in these analyses is the mineralogical make-up of the soils, which may either enhance or neutralise acid generating potential. The results of these analyses also need to be integrated with field observations and placed in a geological and hydrogeological framework, to ensure that laboratory-scale data can be applied for interpretation at the larger landscape scale.

In nature, a number of oxidation reactions of sulfide minerals (principally pyrite: FeS_2) may occur which produce acidity, including:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

$$4FeS_2 + 15O_2 + 10H_2O \rightarrow 4FeOOH + 8H_2SO_4$$

A range of secondary minerals, such as jarosite, sideronatrite and schwertmannite may also form, which act as stores of acidity i.e. they may produce acidity upon dissolution (rewetting). Therefore, any assessment needs to include the presence of such minerals in the material or site.

There is debate as to the most realistic methodology to estimate if a soil will acidify, and the most effective methodology may vary according to the local environment and associated mineralogy of the soil. In this study, we have combined the three most generally accepted methodologies for acid sulfate soil testing:

(i) peroxide pH testing,

(ii) acid-base accounting, and

(iii) incubation (ageing) testing.

These methodologies have different strengths and weaknesses and therefore all have been utilised in the current project. A summary of these methods is presented here.

The current practice in CSIRO Land and Water is to use all of the above techniques and, where possible, to monitor changes in the field during periods of drying to assess the most likely scenarios of acid generation and neutralisation.

Peroxide pH testing

Hydrogen peroxide (H_2O_2) is a strong oxidising agent and is used to encourage the full oxidation of sulfide minerals (principally pyrite: FeS_2), hence the production of acidity. Since peroxide is a very strong oxidising agent, it can be argued that the resultant pH measured is a worst-case scenario, as in nature oxidation is rarely complete. In nature, the presence of carbonate minerals such as calcite ($CaCO_3$) may neutralise acid produced, however, in some cases the carbonate may not fully dissolve due to slow dissolution rates (reaction kinetics) or because of mineral or organic coatings. The dissolution rates of individual minerals may be controlled by a number of factors, hence additional tests based on measuring the carbonate content are recommended.

Acid-base accounting

Acid-base accounting is a technique which balances the potential acid generated (AGP) from sulfide-S (Cr-reducible S or S_{CR}) plus the total actual acidity (TAA) of the soil with the total amount of potential alkalinity (ANC) generated. The ANC is usually only routinely measured when soil pH is greater than 6.5. The net acid generating potential (NAGP) is the acid generating potential (AGP) minus ANC, which gives an indication of expected pH if both react fully.

Arguments against this technique include the fact that the form of carbonate may not be available to soil solutions (e.g. if it is coated and protected with organic material or iron oxides) or if it is in a form which is not particularly reactive (e.g. iron carbonates and dolomite ($CaMgCO_3$) have much slower reaction kinetics than calcite). However, the oxidation of pyrite to insoluble Fe oxides may also cause the pyrite not to react fully if it becomes coated with protective secondary minerals. Thus it may be difficult to assess acidification scenarios effectively.

Acid-base accounting is used to assess both the potential of a soil material to produce acidity from sulfide oxidation and also its ability to neutralise any acid formed (e.g. Sullivan *et al*. 2001, Sullivan *et al*. 2002). The standard acid based accounting applicable to acid sulfate soils is described in Ahern *et al*. (2004) and summarised here. The two equations below show the calculation of net acid (NA) and net acid generating potential (NAGP).

Net Acidity (NA) = Potential Sulfidic Acidity (AGP) + Existing Acidity (TAA) – measured Acid Neutralising Capacity (ANC) / Fineness Factor (FF)

and

Net Acid Generating Potential (NAGP) = Potential Sulfidic Acidity (AGP) – measured Acid Neutralising Capacity (ANC)

Incubation (ageing) testing

This method, which is often considered to represent a more realistic scenario for acid sulfate soil testing, is based on the “incubation” (or ageing) of soil samples. A number of specific techniques are employed, but all are based on keeping the sample moist for a specified period (usually a number of weeks; recent recommendations have increased the period from 8 to 19 weeks), which allows slow oxidation of sulfide minerals to occur. Although this may mimic nature more closely and does not force reactions to occur (as with the peroxide test) or rely on total ‘potential reaction’, it can be argued that the complex processes occurring in the field are not adequately reproduced during this laboratory ageing, e.g. complex processes including exchange with sub-surface waters (containing ANC) or biogeochemical reactions. These factors should also be taken into consideration wherever possible, although often require a thorough understanding of water movement (e.g. groundwater), and are often site and scenario specific.

2.4.2. Mineralogy by X-Ray Diffraction (XRD)

The soil samples and/or minerals samples (e.g. salt efflorescences) were ground in an agate mortar and pestle and either back pressed into steel holders or deposited onto Si low background holders (depending on how much sample was available).

XRD patterns were recorded with a PANalytical X'Pert Pro Multi-purpose Diffractometer using Co K-alpha radiation, variable divergence slit, post diffraction graphite monochromator and fast X'Cellerator Si strip detector. The diffraction patterns were recorded in steps of 0.05° 2 theta with total counting time of 30 minutes, and logged to data files for analysis using HighScore Plus.

2.4.3. Geochemical analysis by X-ray fluorescence spectrometry (XRF)

Selected samples were analysed by X-ray fluorescence spectrometry (XRF) for major elements and trace elements.

Major elements were determined on fused borate glass discs. Approximately 1 g of each oven dried sample (105°C) was accurately weighed with 4 g of 12-22 lithium borate flux. The mixtures were heated to 1050°C in a Pt/Au crucible for 20 minutes to completely dissolve the sample then poured into a 32 mm Pt/Au mould heated to a similar temperature. The melt was cooled rapidly over a compressed air stream and the resulting glass disks were analysed on a PANalytical Axios Advanced wavelength dispersive XRF system using the in-house Silicates calibration program. The calibration was derived from a combination of 192 synthetic and certified reference materials with measured intensities corrected for drift using two highly stable monitor standards.

Trace elements were determined on pressed powder pellets. Approximately 4 g of each oven-dried sample (105°C) was accurately weighed with 1 g of Licowax binder and mixed using a test-tube shaker. The mixtures were pressed in a 32 mm die at 12 tons pressure and the resulting pellets were analysed on a PANalytical Axios Advanced, wavelength dispersive XRF system using the in-house ProTrace calibration.

2.4.4. Rapid metal release analyses

Sample handling and preparation

All soils, whether dry, moist or wet-logged when collected, were dried before use in the rapid (acid, metal and nutrient) mobilisation tests. Slow drying of soils in slightly humid conditions best resembles what may occur naturally in the field, however, due to the relatively short timeframe of the project, standard methods (e.g. Acid Sulfate Soils Laboratory Methods Guidelines) for soil drying and oxidation (e.g. 3 months) were not practical. Instead, the soils were air-dried in a temperature-controlled cabinet at 80 ºC (not fan-forced) for one day. Previous experiments have indicated that the rapid drying of the soils would not result in significant changes to the acidity of the soils (Simpson et al., 2008).

Samples were handled using protocols to avoid sample contamination. This included the wearing of clean powder-free vinyl gloves for the handling of all sample bottles and sampling equipment. All containers used for samples were be either new (in the case of plastic bags and containers), for storage of solid phases, or new and acid-washed (in case of plastic bottles) for handling and storage of water samples. The bottles for analyses of dissolved metals were soaked for 24 hr in 10% nitric acid then rinsed with MQ water and stored dust-free in polyethylene bags.

Rapid acid, metal and nutrient mobilisation assessment methodology

The re-wetting of the soils is expected to occur at different rates at each site and may involve slow or rapid wetting with large or small volumes of water. The fate of the water following re-wetting is unknown and is expected to be different at each site and be greatly affected by the soil properties, including the degree of surface cracking and sub-surface fissures, and land topography. Consequently, a large number of different mechanisms can be envisaged for the mobilisation and transport of various substances from the soils. The substances considered in the current study were acid (pH, alkalinity and acidity changes), anions (chloride and sulfate), nutrients (N and P compounds), carbon, major cations and trace metals. In the different soil types, these substances will be present in different forms and will have differing mobility. Because of the large variety of possible re-wetting scenarios and the variety of soils being considered (surface versus sub-surface soils, desiccated/cracked versus uncracked), some real scenarios may, however, exist where greater substance mobilisation occurs in certain areas.

The acidity, metal and nutrient metal mobilisation experiments are undertaken by shaking the dried soils in oxygenated deionised water to simulate the possible re-wetting of the soils.

The conceptual model for the mobilisation processes assumes:

(i) Soils in the field will be re-wetted by water resulting in release of substances from soil to the associated waters;

(ii) Substance release from soils resuspended in water will be greater than from soils in contact with near-stationary water (as occurs for saturated sub-surface soils);

(iii) The use of deionised water for all rapid-mobilisation tests is proposed as a means of standardising the method and improving site to site comparison of results. The concentrations of major cations and anions (alkalinity and hardness) rapidly released from the soils are expected to greatly outweigh the concentrations of these substances in river water. Consequently, deionised water and River Murray water would be expected to give essentially the same results.

(iv) A 24 h mixing period of soils in oxygenated water should provide sufficient time for the dissolution of the majority (e.g. >80%) of substances from most soils (Simpson *et al*., 2008); and

(v) Above a total suspended solids (TSS) concentration of 100 g/L, the substance release should become relatively independent of TSS concentration (Simpson *et al*., 2008).

Method summary: A soil (TSS) concentration of 100 g (dry weight)/L and mixing period of 24 h will be used for all rapid mobilisation tests. The soils will be resuspended (40 g dry weight in 400 mL deionised water in a 500 mL Nalgene bottle – 100 mL headspace) by rolling the bottles containing soil and water at 100 rpm on a purpose built bottle roller. The water quality parameters, pH, redox potential (Eh), conductivity (EC) and dissolved oxygen will be measured at the start and finish of all tests, and after 6 h for selected tests. After 24 h, the waters will be centrifuged before sample collection. Alkalinity, nutrient (N and P) and major ion analyses will be performed on unfiltered samples (centrifuged and no visible suspended solids present) and dissolved metals analyses will be made on <0.45 µm filtered samples so that they can be accurately compared to the water quality guidelines. The full set of analyses on water samples at the end of the tests will comprise (i) alkalinity (ii) dissolved organic carbon, (iii) the major anions/nutrients (Cl, NO_2, NO_3, PO_4, SO_4), (iv) the major cations Na, K, Ca, Mg, and (v) the trace metals or metalloids Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn.

2.4.5. Water analysis methods

The water samples were immediately transferred to a fridge and kept cool at 4°C until analysed. Major cations and sulfur were analysed on an ARL 3580B Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES). For trace multi-element analysis, water samples are analysed by Inductively Coupled Plasma Mass Spectrometry (ICPMS) [APHA method 3125] on an Agilent 7500ce (Aglient Technologies, Tokyo, Japan). Nitrogen species, Cl and PO_4 were analysed by colorimetric analysis using an Auto analyser, Br, F and SO_4 by ion chromatography and NPOC by a TOC Analyser. Alkalinity analyses were by automated measurement (e.g. PC Titrate) using pH 4.5 for indicating the total alkalinity end-point. Acidity is determined by titration with a standardised alkali to an end-point pH of 8.3.

Moisture content was analysed by gravimetric procedure based on weight loss over a 12-24 h drying period at 110±5ºC. Paste pH was determined on a saturated paste by ISE. Electrical conductivity of saturated soil paste was determined using a saturated paste by ISE (USEPA 600/2-78-054).

2.5. Hazard Assessment

The hazard assessment of acid sulfate soil materials is based on the acidification likely to take place upon drying. The more likely the occurance of acidification, then the greater potential there is for acidification impacts to occur that need to be considered and managed. Inland acid sulfate soils have only in recent years been identified as a potential hazard within the Murray-Darling Basin. This has partly been due to the current drought conditions and low water levels that have exposed sulfidic materials which have subsequently formed sulfuric materials. Case studies in the Lower Lakes and in the channel and adjacent wetlands below Lock 1 (Fitzpatrick *et al*. 2008a) have shown that there are considerable risks of soil acidification due to oxidation of previously unknown acid sulfate soils.

Management options and recommendations for acid sulfate soils have largely been determined for coastal acid sulfate soils (e.g. Dear *et al*. 2002), particularly for the disturbance of these during coastal development. However, the landscape characteristics, impacts and extent of inland acid sulfate soils are often very different from coastal regions and issues including areal extent, access and ecological impacts need to be addressed differently as discussed by Shand *et al*. (2008a).

Two methods for assessing the acid sulfate soil hazard have been used and these are outlined below.

2.5.1. Acid hazard class determined by the lime treatment category

The assessment method of Dear *et al*. (2002) is used as a guide to determine the level of acid sulfate soil problems. Essentially a lime requirement calculation is made and then used to determine the level of treatment required to ameliorate all existing and potential acidity caused from disturbing the soil material. According to Dear *et al*. (2002) there is a general correlation between the “level of treatment required” and “the environmental risk” of the acid sulfate soil as a hazard. The more lime required for treatment the greater the acid sulfate soil is a hazard.

Dear *et al.* (2002) have developed a “Risk categorisation to guide management planning” to assist in “evaluating the environmental risk” posed by acid sulfate soil disturbance by identifying the level of treatment required to treat all existing and potential acidity resulting from such a disturbance. They defined the following five treatment categories: Low, Medium, High, Very High and Extra High based on laboratory results and the weight of material to be disturbed or exposed to air.

According to Dear *et al.* (2002), there is a general correlation between the “level of treatment required” and “the ASS environmental risk”. There are additional factors that will also influence the level of treatment required including the nature of the works to be undertaken, the staging and duration of construction, the soil characteristics (e.g. variability of sulfide concentrations, soil bulk density, physical characteristics such as texture, and self-neutralising capacity), surface and sub-surface hydrology, sensitivity of the surrounding environment, and the past history of the site. As other factors need to be considered, the lime rate values provide are not the final treatment requirements for lime applications, but are a calculated value made within a framework to indicate relative levels of treatment required.

Dear *et al.* (2002) have defined the total amount of fine agricultural lime required to neutralise the total existing plus potential acidity of a particular volume of soil, including the minimum industry safety factor of 1.5. Interpretation of the data and evaluation with Table 2 from Dear *et al.* (2002), identifies the treatment category and acid sulfate soil risk categories for each soil layer.

2.5.2. Acidification, metal mobilisation, and de-oxygenation hazards determined by soil material categorisation

This study has used robust and tested coastal and inland acid sulfate soil assessment methodologies (e.g. peroxide testing, acid-base accounting, water soluble sulfate, soil incubation/ageing and surface and ground water quality measurements) to characterise the acid sulfate soil material types identified in the Finniss River, Currency Creek, Goolwa Channel and Black Swamp areas.

Each acid sulfate soil material type identified may present or has the potential to present a number of environmental hazards, specifically:

- **acidification** (of soil, groundwater and surface waters),
- **metal mobilisation** (from acid sulfate soil material to groundwater and surface water), and
- **deoxygenation** of surface waters.

The hydrogeochemical processes that are responsible for these hazards are inherently linked, in that both acidification and deoxygenation are likely to cause the mobilisation of metals. These hazards may present a **'current'** risk to environmental receptors - where the hazard has been measured or observed, **or** present a **'potential'** risk to environmental receptors - where laboratory analyses of soil properties indicates that a hazard is likely to eventuate if environmental conditions are changed. The general relationship between the acid sulfate soil material types and the hazard condition is presented in Table 2-1.

Table 2-1. General relationships between acid sulfate soil material types and hazard condition.

Type of Acid Sulfate Soil Material	Hazard Type and Condition		
	Acidification	**Metal Mobilisation**	**Deoxygenation**
Sulfuric	current	current	none
Hypersulfidic	potential	potential	none
Hyposulfidic ($S_{CR} \geq 0.10\%$)	potential	potential	none
Monosulfidic (observed)	potential	current	current
Monosulfidic (potential)	potential	potential	potential
Hyposulfidic ($S_{CR} < 0.10\%$)	potential	potential	none
Other acidic (pH_w &/or $pH_{incubation}$) 4 to 5.5 soil materials	current or potential	current or potential	none
Other soil materials	none	none	none

2.6. Rapid Assessment Survey

A rapid acid sulfate soil assessment was conducted in July 2008 using the Murray-Darling Basin Commission 'Acid Sulfate Soils Field Guide', which comprised: (i) field measurements of water quality, (ii) field measurements pH and (iii) collection of soils in chip trays followed by laboratory pH testing before and after incubation. The data collected through this rapid assessment method (Appendix 1) was screened and interpreted by staff in CSIRO using agreed criteria and the information communicated to staff in the Murray-Darling Basin Authority and Department of Environment and Heritage (South Australia).

2.7. Follow-up Surveys

Several follow-up surveys and sampling of soils, salt efflorescence's and waters were conducted mainly at Wally's Landing from December 2008 to May 2009 – using standard field and laboratory procedures as described for Phase 1 acid sulfate soil assessment.

3. RESULTS

This section identifies the sites and describes the general features of the soil morphology and laboratory data for the study area. A more detailed analysis is provided in the following sections for each of the geographic areas, which compares the different methodologies applied and assesses the likelihood of acid generation due to acid sulfate soils.

Field survey work was conducted between 18th and 26th November 2008. During this time 39 sites were visited and 143 soil layers described and sampled. Laboratory analysis for pH testings and acid based accounting were conducted during November through to January, with the more detailed analysis of $pH_{incubation}$, metals and mineralogy conducted on selected samples from February through to May.

In addition, selected follow-up surveys and sampling of soil materials and waters were conducted from December 2008 to May 2009, essentially to capture the sequential changes and transformations in acid sulfate soil materials due to continuous:

(i) drying of acid sulfate soil materials caused by lowering of water levels from deep-water acid sulfate soil to subaqueous acid sulfate soil to waterlogged/saturated acid sulfate soil and finally to drained/unsaturated acid sulfate soil classes with sulfuric material (pH < 4) in the upper soil layers (Figure 1-2) and

(ii) re-wetting of acid sulfate soil materials caused by winter rainfall re-flooding events in the catchments.

The study area is adjacent to Lake Alexandrina in the lower reaches of the River Murray in South Australia (Figure 1-1). For purposes of describing data and interpretations in this report the study area has been separated into four geographic areas that are: Finniss River, Currency Creek, Black Swamp and Goolwa Channel.

The site identification numbers and locations are listed for each of the areas in Table 3-1. A detailed listing of the site information along with the descriptive profile data is provided in Appendix 3.

Table 3-1. Site identification number, locality, depth to water table, and surface condition separated into each of the geographic areas in the study region.

Where: Site Identification Number (CUR – currency creek area, FIN – Finniss river area), site co-ordinates (WGS 84 Zone 54), depth to water table (soil surface is ‘0’, if value is ‘+ve’ then water level is below surface, if ‘-ve’ then water level is above surface, NR indicates water level ‘not reached’), soil surface condition, surface earth cover (either water, vegetation type or bare – no vegetation).

Site ID Number	Sampled Date	Easting_ zone54H	Northing_ zone54H	Depth to Water Table (cm)	Surface Condition	Earth Cover (Vegetation type)
Goolwa Channel						
CUR11	18/11/2008	302384	6070538	-10	water	water
CUR12	18/11/2008	302365	6070521	NR	sealed	bare, few weeds
CUR13	18/11/2008	302272	6070678	80	cracking	bare
CUR14	18/11/2008	302218	6070463	NR	sealed	weeds
CUR15	18/11/2008	305343	6071064	NR	sandy, firm	bare
CUR16	18/11/2008	305395	6070954	-10	water	water
CUR17	18/11/2008	305334	6071123	NR	sealed, peaty	bare

Site ID Number	Sampled Date	Easting_ zone54H	Northing_ zone54H	Depth to Water Table (cm)	Surface Condition	Earth Cover (Vegetation type)
CUR18	18/11/2008	305224	6071431	NR	sandy, firm	bare
CUR19	18/11/2008	305152	6071684	NR	sandy, firm	few reeds nearby
Currency Creek						
CUR20	19/11/2008	298356	6073698	-40	water	water
CUR21	19/11/2008	298352	6073708	60	sealed	bare
CUR22	19/11/2008	298350	6073695	NR	sealed	bare
CUR23	19/11/2008	298538	6073748	1	sealed	bare
CUR24	19/11/2008	298557	6073753	-30	water	water
CUR25	19/11/2008	298414	6073793	NR	sealed, salt crust	bare
CUR26	19/11/2008	301098	6072836	-20	water	water
CUR27	19/11/2008	301049	6072909	NR	sealed, sandy	bare
CUR28	19/11/2008	301047	6072912	NR	sealed, sandy	bare
Finniss River						
FIN20	20/11/2008	305780	6073935	45	cracking	bare
FIN21	20/11/2008	305888	6073941	55	cracking	bare
FIN22	20/11/2008	305945	6074053	-10	water	water
FIN23	20/11/2008	305748	6074053	NR	cracking	bare
FIN24	20/11/2008	305756	6074049	NR	cracking	bare
FIN25	20/11/2008	305810	6074047	55	soft, peaty	bare
FIN26	20/11/2008	303084	6079608	30	sealed, salt	bare
FINx	20/11/2008	305720	6073883	0	water	water
FIN27	22/11/2008	306196	6075060	NR	sealed, soft	bare
FIN28	22/11/2008	305974	6075099	NR	cracking, hard	bare
FIN30	26/11/2008	307978	6073636	-30	water	water
FIN31	26/11/2008	308016	6073669	60	sealed, sandy	bare
FIN32	26/11/2008	308051	6073691	85	loose, sandy	reeds
FIN33	26/11/2008	306784	6076264	NR	loose, sandy	phragmities
FIN34	26/11/2008	306777	6076255	NR	sealed	bare
FIN35	26/11/2008	306748	6076232	50	peaty, soft	bare
FIN36	26/11/2008	306736	6076216	-20	water	water
FIN37	26/11/2008			NR	sealed, sandy	bare
FIN38	26/11/2008	304329	6079422	45	peaty, soft	bare
FIN39	26/11/2008	304300	6079424	-3	water	Water
Black Swamp						
FIN29	22/11/2008	302739	6076943	-20	water	reeds

3.1. Soil Morphology

A detailed listing of the site information along with the descriptive profile data is provided in Appendix 3. Soil colour, texture, structure and consistency are valuable field indicators for soil identification and appraisal. Soil type can determine potential impacts on acid sulfate soil formation during desiccation or inundation, and likely products of oxidation based on acid generating and acid neutralising characteristics. Sandy or quartz-rich soils are often more at risk of acidification because they have little capacity to neutralise acidity, whereas clay-rich soils have ability to neutralise acidity through dissolution of clay minerals. Individual soil profiles often show variations in layer textures, contributing to the complexity of interpreting likely acid sulfate soil behaviour at each site.

The soil textures where commonly clayey, and in some areas individual soil profiles show variations in texture between layers. The clayey soils tended to occur in the lower landscape positions in association with water or in the subsoils, whereas the sandy textures tended to be higher in the landscape often near reeds and where wind blown sand would accumulate. The soil matrix colour was mainly dark greys, but other colours ranged from black to pale greys, and brownish greys. The colours are indicative of the reduction-oxidation state of the soil, and the predominance of darker colours particularly in the subsoils indicated reducing or anaerobic conditions. Soil mottle colours where found in the upper subsoils and generally where pale yellowish colour occur low pH values (< 4) were measured indicating jarosite or natrojarosite. Most wet or moist soils were structureless, but where the surface and upper subsoil layers had dried by the lowering water levels deep desiccation cracks develop, which usually form large trans-horizon polygonal cracks with columnar ped structures. These cracking soils were a dominant feature in some parts and associated with them were prominent salt efflorescences and precipitates on the ped surfaces (upper and down cracks) consisting of a range of minerals identified as jarosite, natrojarosite, schwertmannite, sideronatrite and other soluble Al-Fe-Mg-Na sulfates.

Soil colour, texture, structure and consistency provide field observable indicators of soil redox status and existing acidity. Consequently, these field indicators were used to contribute to the development of the user-friendly soil identification key to categorise the various acid sulfate soil subtypes (Fitzpatrick *et al.* 2009b).

The combination of soil morphological features allowed similar soil layers to be matched between different sites. A number of sites were generally placed in a transect stretching from the water to the higher landscape position. By observing the site landscape position and correlation of soil layers between sites, a conceptual soil toposequence is constructed that shows the surveyors understanding of how the soil varies across an area by integrating what is seen at multiple sites. These conceptual soil toposequence models are a powerful tool to provide an understanding of how the soil materials change in the landscape and hence how the various acid sulfate soil materials may be distributed across landscapes. Soil toposequence models have been constructed for each of the geographic areas and will be used to describe the vertical and horizontal changes in acid sulfate soil materials across a wide range of landscapes in the following sections.

3.2. Soil Laboratory Data

There is a total of 39 sites described of which laboratory analysis was conducted on 119 soil samples from 33 sites and the results are listed in Appendix 4 and 5. In other 6 sites did not have soil analysis conducted on them (CUR22, CUR24, FIN22, FIN34, FIN37 and FINx), these sites were sampled for either water or mineralogical analyses.

A summary of the results for the soil laboratory data for pH testing and sulfate chemistry is presented in Table 3-2.

Table 3-2. Laboratory data summary for pH testing and sulfate chemistry for all samples.

Parameter	Description	Units	Minimum	Median	Maximum	No. of Samples
EC	Electrical conductivity	mS/cm	<0.01	5	756	119
pH_w	pH in water		2.00*	5.80	8.60	119
pH_{FOX}	pH after peroxide treatment		1.00	1.87	7.59	119
$pH_{incubation}$	pH after ageing 20 weeks		1.00	3.00	7.90	119
pH_{KCl}	pH in KCl		2.89	5.45	9.48	119
Sulfate		mg SO_4 / kg	112	2700	109650	119
TAA	Total actual acidity	mole H^+/ tonne	0	6	2420	119
ANC	Acid neutralising capacity as %$CaCO_3$	mole H^+/ tonne	0	0	3563	119
S_{CR}	Cr-reducible sulfur	mole H^+/ tonne	3	89	2696	119
NA	Net acidity; retained acidity not included	mole H^+/ tonne	-2277	72	2575	119
Lime Calculation	Calculated, with a 1.5 safety factor	kg $CaCO_3$/ tonne	-171	5	193	119

*Several salt efflorescences, surface precipitates and sandy surface materials adjacent to streamlines in wetlands near Wally's Landing (e.g. FIN 26 sites), which underwent rewetting from rainfall events in May 2009 measured pH levels of 0.5 to 1.3 in the field and laboratory.

3.2.1. Soil pH testing (pH_W, pH_{FOX} and $pH_{incubation}$)

A histogram showing the distribution of samples for pH_W, pH_{FOX} and $pH_{incubation}$ is presented in Figure 3-1 and the data is listed in Appendix 4.

The pH_w values indicate that 40 of the 119 samples (34%) of samples are below pH 4.0, and would be characterised as sulfuric material. The pH_{FOX} values indicate that 83 of the 119 samples (70%) of samples are below pH 2.5, and could be characterised as hypersulfidic material. This is supported by the $pH_{incubation}$ values, which indicate that 77 of the 119 samples (65%) are below pH 4.0, and should be characterised as hypersulfidic material.

There are 33 sites that had multiple layers analysed. 18 sites contain a sulfuric material layer and of the remaining 15, they all contain at least one hypersulfidic material layer indicating the strong potential to acidify when exposed to air (oxygen) under moist conditions. All sites contain layers with acid sulfate soil materials.

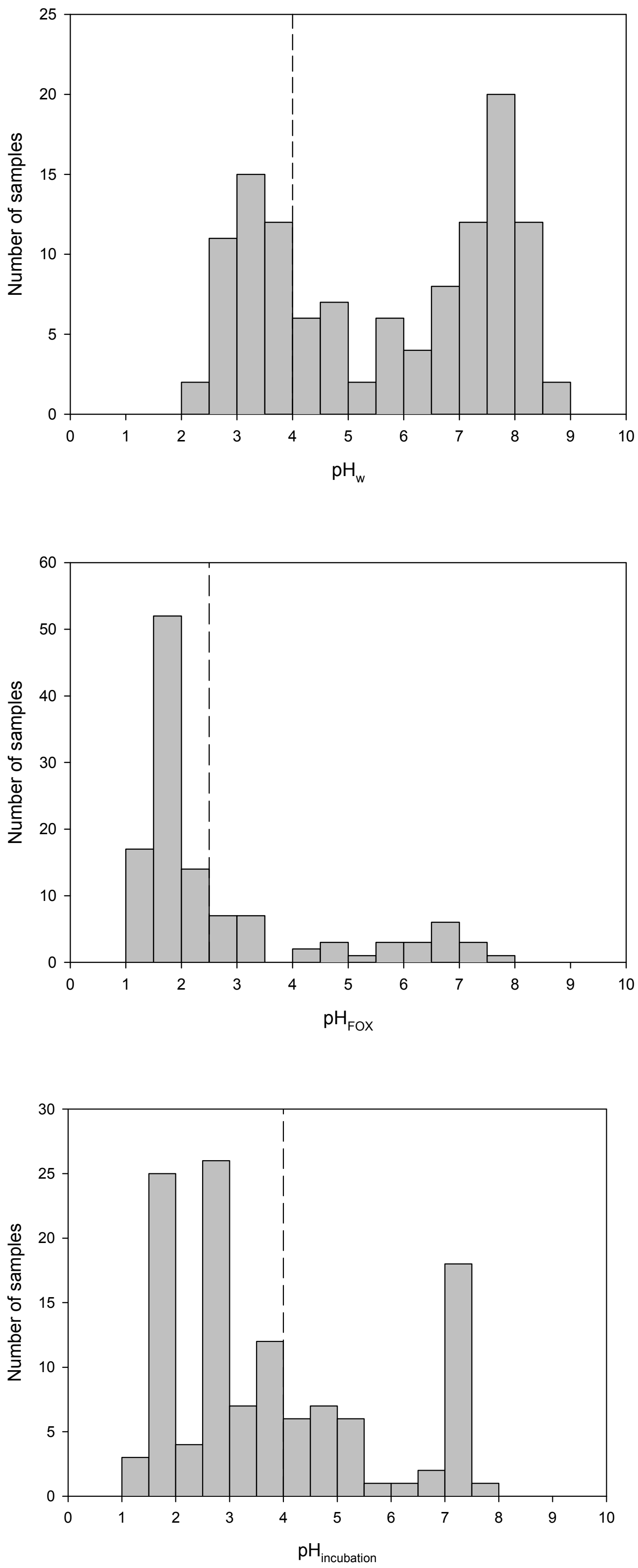


Figure 3-1: Histogram of the pH_w, pH_{FOX}, $pH_{incubation}$ data for all samples.

The critical pHw and $pH_{incubation}$ value of 4.0 and critical value for pH_{FOX} of 2.5 are shown in the respective graphs as a dashed line.

3.2.2. Sulfur chemistry and acid base accounting

Water extractable sulfate values are summarised in Table 3-2 and listed in Appendix 5. The results show all samples have very high sulfate values exceeding 100 mg SO_4 /kg of soil.

All samples contain detectable concentrations of iron sulfide as shown by the summary of chromium reducible sulfur (S_{CR}) in Table 3-2.

The pH_{KCl} data summarised in Table 3-2 and presented in Figure 3-2 show that 75 of the 119 soil samples, 63%, are less than pH_{KCl} of 6.5, and therefore contain zero ANC. The remaining samples range from an ANC of 0 to 3563 mole H^+/tonne.

Net acidity (NA) calculations show that the values range greatly from -2277 to 2575 mole H^+/tonne. With positive values for 90 of the 119 samples, 76%, indicating that samples either contain existing acidity and / or have the potential to further produce acid as they oxidise.

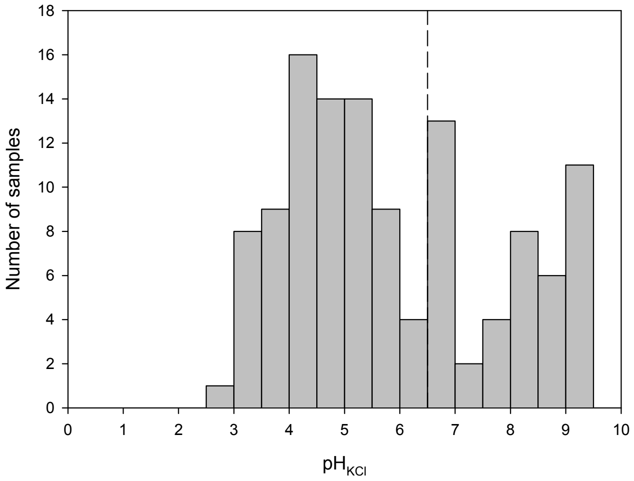


Figure 3-2: Histogram of the pH_{KCl} data for all samples.

The critical pH_{KCl} value of 6.5 is shown as a dashed line.

3.3. Hydrogeochemistry

Seventeen water samples were collected from 15 of the study sites: 10 sites from the creeks and rivers in the channels, one from cracks in the dried wetland, and four from soil pits. The data is presented in Appendix 7.

It should be noted that some chemical parameters and concentrations show short (event based) and medium temporal (e.g. seasonal) variations. This summary represents only a snapshot during the period of sampling. The data presented provide a baseline with which to monitor future change.

The channel waters in the Currency Creek and Finniss River were both alkaline (pH 7.84 and 8.89) with very high SEC or EC values (23,591 and 18,388 µS/cm). The pH of the water in Black Swamp was 7.13. Alkalinity (as HCO_3) was also high in the western part of Currency Creek (175 to 280 mg/L HCO_3) and the waters were oversaturated with dissolved oxygen (DO). However, downstream at site CUR26, the alkalinity was lower at 117 mg/L. The water in the cracks and in the soil pits was very acidic and oxidising (Eh > 500 mV), typical of strongly oxidising conditions associated with sulfuric materials and acid mine drainage. As expected the water also had very high SEC (EC). Alkalinity at pH values below 6.3 is usually zero.

Waters from soil pits in the dry river-beds and wetlands of Currency Creek (with deep cracks) and Finniss River (sands) have pH values ranging from 3.4 to 3.9. Some river waters sampled in Currency Creek and Tookayerta Creek/Black Swamp contain relatively low levels of alkalinity (<117 mg/L and 31 mg/L respectively as HCO_3). Acid sulfate soil influence on the low alkalinity in Currency Creek is likely when compared to the high alkalinity of Lake Alexandrina water (currently in the range 200 to 250 mg/L). This is because the lower Finniss River and, until recently, Currency Creek are contiguous with Lake Alexandrina via the Goolwa channel and should therefore have similar alkalinities. Even with the retreat of the lakes sporadic movement of lake water up the lower Finniss and Currency channels occurs through wind activity, “seiching”. The alkalinity of Lake Alexandrina acts to increase the alkalinity of the remnant Currency Creek and Finniss River waters, along with local contributions from ground waters and evapo-concentration.

3.4. Rapid Mobilisation Tests

The oxidation of these soils has the potential to cause environmental degradation through the release of acidity, nutrients and metals. This study investigated the mobilisation of these substances following the simulated rewetting of dried soils with deionised water.

SUMMARY

The release of nitrate and phosphate from the dried soils was low.

The metal release was rapid and dissolved concentrations of Al, Cd, Co, Cu, Cr, Mn, Ni, V and Zn greatly exceeded the Australian water quality guidelines (WQGs) for protection of ecosystem health.

For Al, Cd, Co, Cu, Cr, Ni and Zn, the concentrations were often greater than 100×WQGs values.

Greater concentrations of metals were released from Finniss River soils than from Currency Creek soils.

The dissolved metal concentrations, released from the soils to the water, were generally significantly greater when the soil-water mixture had pH <5.

3.4.1. Water quality during mobilisation tests

The pH of the waters in which soils were resuspended was, on average, lower for soils from the Finniss River (mean±standard deviation = 4.7±1.6) than soils from Currency Creek (5.2±1.6). The pH was generally lower for soils collected from the upper reaches of each catchment; consistent with greater drying and oxidation of the soils having occurred in the upper catchment. When flowing, historically, these two water bodies would be expected have a water pH in the range 7.0-8.0.

When collected from the field, 12% of the soils had paste-pH values <3, 36% had pH <4, 46% had pH <5, 53% had pH <6, 63% had pH <7, and 88% had pH <8. Following 24-h resuspension of the soils deionised water, 4% had pH <3, 34% had pH <4, 62% had pH <5, 71% had pH <6, 82% had pH <7, and 97% had pH <8. There was a weak relationship between the paste-pH of the soils (following collection) with pH of water upon 24 h of resuspension in deionised water as shown in Appendix 8 (Figure A1a). This relationship was not as strong as observed by Simpson et al. (2008) for similar tests undertaken on a wide range of soils from the River Murray and Lower Lakes system.

The pH, redox potential (Eh), specific electrical conductance (SEC) and dissolved oxygen (DO) concentrations measured at the completion of the mobilisation tests are shown in Appendix 8 (Tables A8.1-A8.4). For all the tests the dissolved oxygen concentrations were >4 mg/L at the completion of the 24-h resuspension period. The relationships between redox potential and pH and dissolved oxygen concentration of waters following 24 h of resuspension in deionised water were weak (Appendix 8, Tables A8.1-A8.4, Figures A8.1b,c). The specific electrical conductance (SEC) of the waters in which soils were resuspended ranged from 0.1-22 mS/cm. The soils from the Finniss River generally resulted in greater SEC than soils from Currency Creek; with mean±standard deviation of 3.5±5.3 mS/cm and 1.9±3.0 mS/cm for the soils samples from Finniss River and Currency Creek, respectively. When flowing, historically, these two water bodies would be expected to have a SEC in the range 0.1-1 mS/cm.

3.4.2. Mobilisation of acid, major anion and cations, and nutrients

At the completion of the 24-h resuspension period the waters were generally acidic (Appendix 8, Tables A8.5-A8.8, Figure A8.2a). The soils from the Finniss River resulted in greater water acidity (mean±SD: 400±1700 mg $CaCO_3$/L) than the Currency Creek soils (60±80 mg $CaCO_3$/L). The greatest acidity of 10,200 mg $CaCO_3$/L was measured for the soil sample FIN26.1.

The concentrations of chloride and sulfate released during in the mobilisation tests were generally much greater than historical concentrations for water in the Finniss River and Currency Creek systems. Historically, chloride and sulfate concentrations of the Finniss River and Currency Creek would be expected to be within the range 100-1000 mg Cl/L and 20-200 mg SO_4/L range, respectively. In the waters from the mobilisation tests, the concentrations were (mean±standard deviation) 600±1600 mg SO_4/L and 330±550 mg Cl/L for the tests of Finniss River soil samples and 1600±3600 mg SO_4/L and 860±1400 mg Cl/L for the tests of Currency Creek soil samples. The highest concentrations of chloride and sulfate measured in the mobilisation tests were 6,200 mg Cl/L and 21,500 mg SO_4/L, respectively (Tables A8.5-A8.8). These results were consistent with significant release of sulfate through the oxidation of the ASS. Sulfate concentrations were often high and there was a strong relationship with the total sulfate concentration in the soil (Figure 3-3 a). The dissolved chloride and sulfate concentration were well correlated (Figure A8.2b). The concentrations of major cations (Na, K, Ca, Mg) released during in the mobilisation tests varied considerably (Appendix 8, Tables A8.9-A8.12). The mobilised major cation concentrations were greater from the Finniss River soil samples (mean±SD: 620±990 mg Na/L, 31±44 mg K/L, 140±220 mg Ca/L, 220±430 mg Mg/L) than concentrations mobilised from Currency Creek soil samples (260±520 mg Na/L, 20±30 mg K/L, 80±160 mg Ca/L, 70±180 mg Mg/L). There were strong relationships between the amount of K, Ca, and Mg released from the soils (Figure 3-3 b).

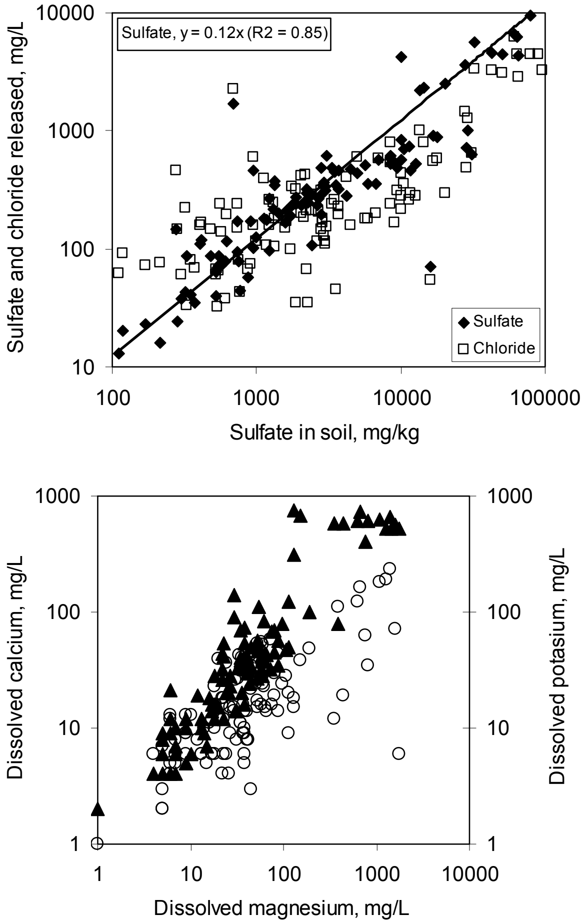


Figure 3-3: Relationship between (a) total sulfate in the soils and dissolved sulfate following 24-h resuspension of soils in deionised water, and (b) dissolved K, Ca and Mg released from the soils.

The total nitrate and phosphate concentrations of the Finniss River and Currency Creek are (historically) <0.1 and <0.01 mg/L, respectively. The concentrations of total N (nitrate+nitrite) and phosphate measured at the completion of the mobilisation tests were generally low, i.e. 0.1-0.5 total-N/L and <0.1 mg PO_4/L (Appendix 8, Tables A8.5-A8.8). The highest concentrations were 21 mg total N/L and 2.8 mg PO_4/L, respectively. The TOC concentrations of the waters measured at the completion of the mobilisation tests were (maximum, mean±standard deviation) 236 (27 ± 43) mg/L. The total organic carbon (TOC) released from the soils from the Finniss River was generally greater (mean±SD: 35±54 mg/L, <1-236 mg/L range) than soils from Currency Creek (mean±SD: 18±23 mg/L, 2-139 mg/L range). There was a reasonably good log-log relationship between the dissolved calcium and magnesium concentrations released from the soils (Appendix 8, Figure A8.3a).

3.4.3. Release of trace metals and metalloids from soil samples

The concentrations of trace metals and metalloids released from the soils samples in the mobilisation tests are shown in Appendix 8 (Tables A8.13-A8.16). The mean±SD and maximum concentrations for each element are shown in Table 3-3. These concentrations can be compared to the metal concentrations measured in the River Murray and the lower lakes sites of Meningie and Milang (Simpson et al., 2008) (Table 3-4). The concentrations of Al, Fe and Mn released from the soils to the waters were very high, with concentration of 2100 mg Al/L, 700 mg Fe/L and 770 mg Mn/L for one soil. For the trace metals, there were also some very high concentrations. In general, the order of greatest release was Co>Ni>Zn>Cu>Cr and V>As>>Pb, Ag, Se, and Sb (Table 3-3). There were strong correlations between many of the released metals (Appendix 8).

There were exceedances of the guidelines in the metal mobilisation tests for all metals for which Australian WQGs exist (e.g. Table 3-4). It is important to note that the metal mobilisation tests were expected to result in a worst case scenario for rapid metal release from most of these soils (undertaken using high concentrations of suspended solids (100 g/L) with the soils shaken for 24 h).

The number of WQG exceedances after applying a dilution factor (10×, 100×, 1000×), expected for these waters mixing with river or lake water, has also been calculated. For the Currency Creek samples, the metals that most often exceeded the WQGs were Co (78% of 54 samples), Al (76%), Cu (74%), Zn (56%), Ni (50%), Cr (37%), V (30%), and Cd (24%) (Table 3-5). Based on the maximum dissolved concentrations following dilution, the metals most greatly exceeding the WQGs by 10× were Co (52% of 54 samples), Al (41%), Zn (15%), Ni (6%), and Cd, Cr, Cu (4% each). The metals exceeding the WQGs by 100× were Co (20% of 54 samples) and Al (4%),. The metals exceeding the WQGs by 1000× were Al and Co (2% of 54 samples).

For the Finniss samples, the metals that most often exceeded the WQGs were Co (78% of 54 samples), Cu (74%), Al (61%), Zn (56%), Ni (50%), Cr (37%), V (30%), and Cd (24%) (Table 3)Cd (51%) and Mn (51%) (Table 3-5). Based on the maximum dissolved concentrations following dilution, the metals most greatly exceeding the WQGs by 10× were Co (68% of 57 samples), Al (47%), Zn (33%), Cu (25%) and Ni (19%), Cd (14%), Cr (12%), V (11%) and Mn (9%). The metals exceeding the WQGs by 100× were Al (81% of 57 samples), Co (40%), Al (23%), Zn (7%), Cr and Ni (4%) and Cu and Cd (2%). The metals exceeding the WQGs by 1000× were Co (18% of 57 samples) and Al (11%).

Greater concentrations of metals were released from Finniss River soils than from Currency Creek soils. In general, the concentrations of (i) Al, Fe and Mn (Figure 3-4), and (ii) Co, Ni, Zn, Cu, Cr and V (Figure 3-5) released from Finniss River and Currency Creek soils samples were observed to increase greatly at pH <5. Concentrations of vanadium displayed a minimum near pH 5, partly to do with it behaving as an anion at higher pH values.

In general, the frequency by which dissolved metal concentrations, released from the soils to the water, exceeded 10× the WQG concentrations was much greater below pH 5 (Figure A8.4 and A8.5). While a detailed analysis of the metal release processes has not been undertaken with respect to the soil properties, initial analyses indicates that there is a weak relationship between the total actual acidity (TAA) of the soils and the concentrations of aluminium and sulfate released from the Currency Creek (●) and Finniss River (□) soils (Figure 3-6).

Table 3-3: Concentrations of trace metals and metalloids mobilised from Currency Creek and Finniss River soil samples: mean±standard deviation (maximum, minimum).

Currency Creek	**Al, mg/L**	**Fe, mg/L**	**Mn, mg/L**
Mean	3.3	3.3	1.3
Standard deviation	**11**	63	**3.4**
Maximum	**73**	370	**22**
Finniss River	**Al, mg/L**	**Fe, mg/L**	**Mn, mg/L**
Mean	**48**	24	6.0
Standard deviation	**280**	96	**16**
Maximum	**2100**	700	**77**
WQG (95% PC) [a]	**0.055**	**NV**	**1.9**

	Trace metals and metalloids, µg/L											
Currency Creek	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Sb**	**Se**	**V**	**Zn**
Mean	0.012	4.9	**0.38**	**230**	**1.7**	**2.9**	**36**	0.77	0.1	0.7	5.7	**44**
Standard deviation	0.009	8.5	**1.1**	**1000**	**2.9**	**3.9**	**83**	1.9	0.1	1.2	**7.5**	**88**
Maximum	**0.070**	**54**	**7.4**	**7500**	**18**	**22**	**530**	**6.0**	0.7	6.4	**378**	**480**
Finniss River	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Sb**	**Se**	**V**	**Zn**
Mean	0.025	9	**1.8**	**640**	**22**	**30**	**159**	1.6	0.1	0.5	**21**	**250**
Standard deviation	0.055	**20**	**3.9**	**1100**	**130**	**130**	**430**	3.2	0.1	0.7	**46**	**570**
Maximum	**0.370**	**140**	**21**	**4900**	**970**	**950**	**2700**	**18**	0.6	3.5	**240**	**2900**
WQG (95% PC) [a]	**0.05**	**13**	**0.2**	**1.4**	**1.0**	**1.4**	**11**	**3.4**	**NV**	**11**	**6.0**	**8.0**

[a] Water quality guideline, 95% level of ecosystem protection (without hardness corrections etc) in ANZECC/ARMCANZ (2000).

The WQG for As assumes all is as As(V), which is less toxic than As(III) (WGQ = 24 µg/L). The WQG for Cr assumes all is as Cr(VI). The WQGs for Co and V are low reliability values. Exceedances of guidelines are in **bold.** Guidelines for A, Fel and Mn are shown in mg/L.

Table 3-4: Metal concentrations in the River Murray and the lower lakes sites of Meningie and Milang (from Simpson et al 2008).

Site	**Ag µg/L**	**As µg/L**	**Cd µg/L**	**Co µg/L**	**Cr µg/L**	**Cu µg/L**	**Mn µg/L**	**Ni µg/L**	**Pb µg/L**	**Se µg/L**	**V µg/L**	**Zn µg/L**
River Murray	0.07	0.6	<0.05	<0.1	<0.1	0.8	2	0.6	<0.1	<0.2	0.5	4.5
Wellington	<0.02	0.8	<0.05	<0.1	<0.1	0.8	<1	0.6	<0.1	<0.2	1.3	0.6
Meningie	**0.08**	3.1	<0.05	0.6	0.8	**2.5**	38	3.1	1.1	<0.2	5.6	2.8
Milang	0.11	1.9	<0.05	0.1	0.2	0.5	1.7	1.2	<0.1	<0.2	2.2	1.9
WQG (95% PC) [a]	**0.05**	**13**	**0.2**	**1.4**	**1.0**	**1.4**	**1900**	**11**	**3.4**	**11**	**6.0**	**8.0**

[a] Water quality guideline, 95% level of ecosystem protection (without hardness corrections etc) in ANZECC/ARMCANZ (2000). The WQG for As assumes all is as As(V), which is less toxic than As(III) (WGQ = 24 µg/L). The WQG for Cr assumes all is as Cr(VI). The WQGs for Co and V are low reliability values. Exceedances of guidelines are in **bold**.

Table 3-5: Water quality guidelines (WQG) and number of exceedances of WQG for Currency Creek and Finniss River samples.

Site	Al	Ag	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Se	V	Zn
WQG, µg/L[a]	**55**	**0.05**	**13**	**0.2**	**1.4**	**1**	**1.4**	**1900**	**11**	**3.4**	**11**	**6**	**8**
Currency Creek													
# >WQG	54	1	4	13	48	20	32	6	27	2	0	16	28
% of total (of 54)	76%	2%	7%	24%	89%	37%	59%	11%	50%	4%	0%	30%	52%
# >10× WQG	54	0	0	2	27	2	2	1	3	0	0	0	8
% of total (of 54)	41%	0%	0%	4%	50%	4%	4%	2%	6%	0%	0%	0%	15%
# >100× WQG	42	0	0	0	11	0	0	0	0	0	0	0	0
% of total (of 54)	7%	0%	0%	0%	20%	0%	0%	0%	0%	0%	0%	0%	0%
# >1000× WQG	44	0	0	0	1	0	0	0	0	0	0	0	0
% of total (of 54)	2%	0%	0%	0%	2%	0%	0%	0%	0%	0%	0%	0%	0%
Finniss River													
# >WQG	54	5	7	25	46	21	28	14	37	8	0	22	37
% of total (of 57)	61%	9%	12%	44%	81%	37%	49%	25%	65%	14%	0%	39%	65%
# >10× WQG	54	0	1	8	39	7	14	5	11	0	0	6	19
% of total (of 57)	47%	0%	2%	14%	68%	12%	25%	9%	19%	0%	0%	11%	33%
# >100× WQG	46	0	0	1	23	2	1	0	2	0	0	0	4
% of total (of 57)	23%	0%	0%	2%	40%	4%	2%	0%	4%	0%	0%	0%	7%
# >1000× WQG	35	0	0	0	10	0	0	0	0	0	0	0	0
% of total (of 57)	11%	0%	0%	0%	18%	0%	0%	0%	0%	0%	0%	0%	0%

[a] WQG, 95% level of protection (without hardness corrections etc) as per earlier Table. [b] For Al, the limit of reporting (LOR) was 100 µg/L and above the WQG of 55 µg/L. Where the dissolved Al concentration was <LOR, it is considered <WQG, although in some case sit may exceed the WQG.

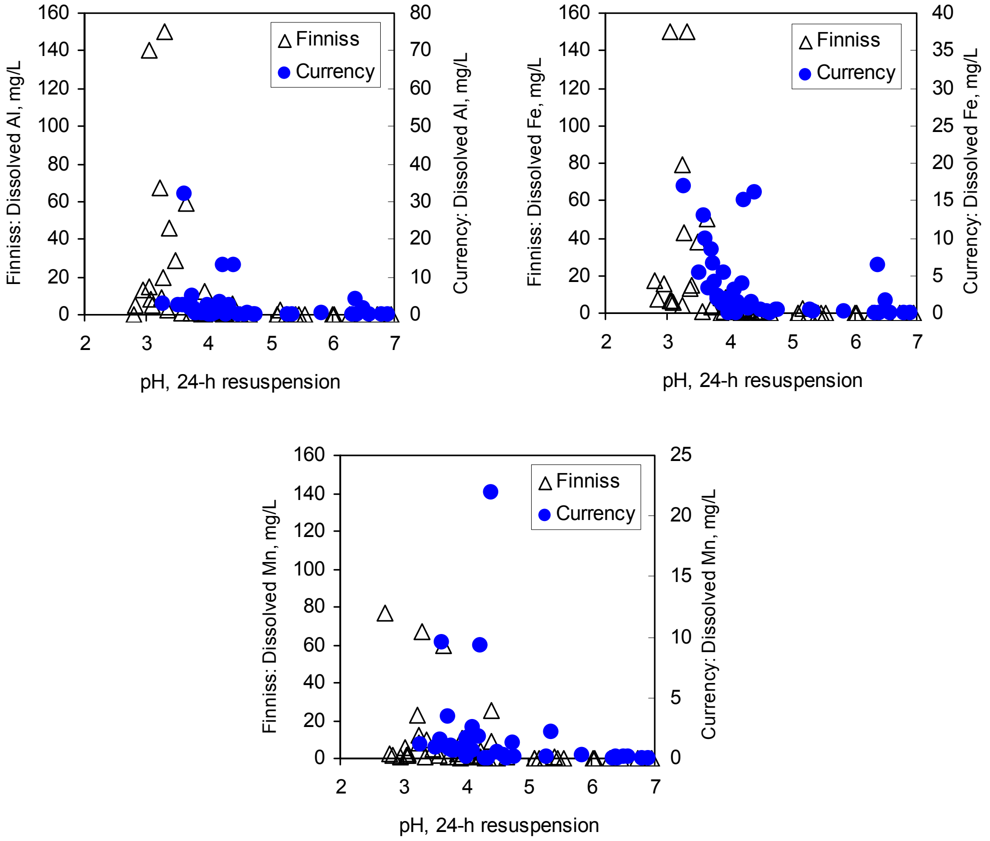


Figure 3-4: Relationship between pH of water and concentrations of Al, Fe and Mn released from Finniss River and Currency Creek soils samples following 24 h of resuspension of soils in deionised water.

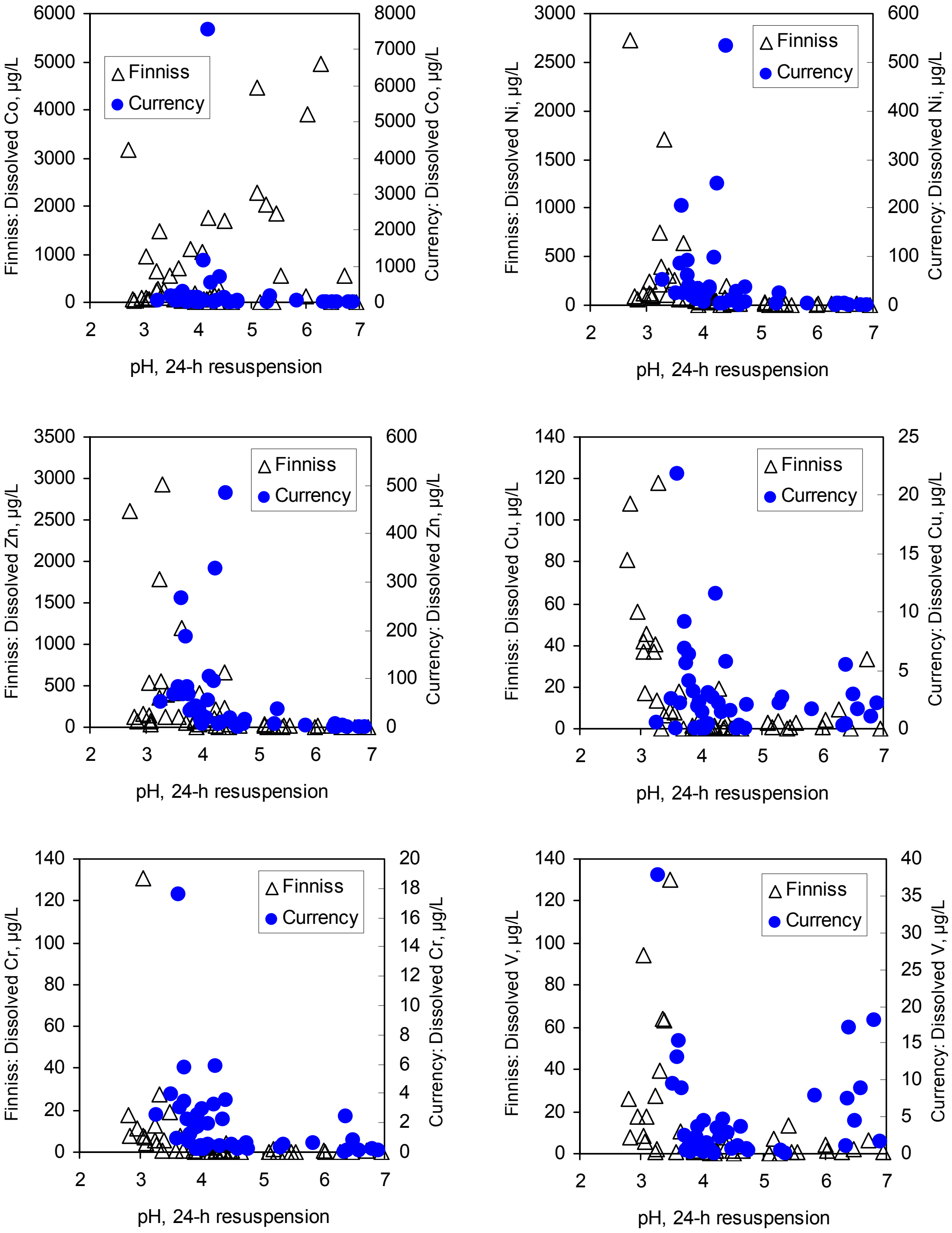


Figure 3-5: Relationship between pH of water and concentrations of Co, Ni, Zn, Cu, Cr and V released from Finniss River and Currency Creek soils samples following 24-h resuspension of soils in deionised water. Note: some maximum concentrations (e.g. FIN26.1) are off-scale and note shown (Appendix 8, Tables A8.13-A8.16).

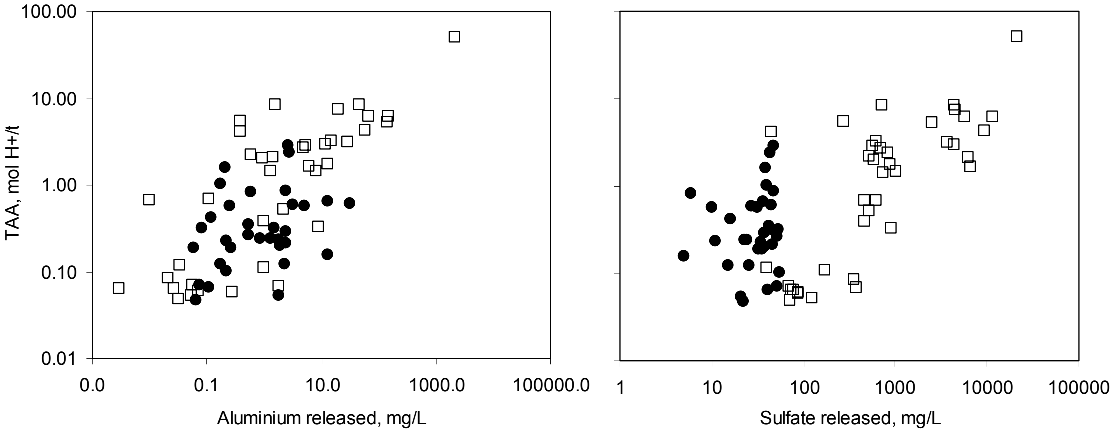


Figure 3-6: Relationship between total actual acidity (TAA) of the soils and the concentrations of aluminium and sulfate released from the Currency Creek (●) and Finniss River (□) soils.

3.5. Mineralogy of Soil Materials, Salt Efflorescence's and Surface Precipitates

The mineralogy of selected soils was determined by X-ray diffraction (XRD). See Appendix 9 for mineral identification interpretation inserted on each X-ray diffraction pattern and photographs. The occurrence of the minerals is discussed as part of the study area description in sections below.

3.6. X-Ray Fluorescence Analysis of Soil for Major and Minor Elements

Element analysis for the soils of the Currency Creek and Finniss River areas is potentially important. Both of these systems drain catchments which have a high proportion of agricultural activity and cross Kanmantoo series rocks which are known to have concentrations of both pyrite and mineral ore bodies.

For the major elements (see Appendix 9), analyses indicate that the concentrations are considered to be in the natural range (Bowen 1979). Several sites with high organic matter or peat (e.g., CUR 11, 13 and 17) show relatively high phosphorus concentrations in the upper layers. Iron and aluminium concentrations are highly correlated. Except for layers which have strong calcium carbonate accumulations, the calcium to magnesium ratios usually decrease with depth. These observations are not unusual in these environments.

Although there are several anomalies among the minor elements (Appendix 9), in general total concentrations for most elements are in the normal range for soils. The lower limits for detection using X-ray fluorescence analysis for elements such as Cd and Hg are too high to be useful and these elements require specialist analysis. As expected, concentrations are higher in clayey soils than in the sandy soils.

Several values for Br and I are high, but are clearly related to high Cl concentrations and are geochemically related through cyclic salts of marine origin. Iron and manganese are also geochemically related and probably reinforced in these environments by redox conditions. Co is anomalously high in many sites and its concentration is not related to Fe. Co is an element of interest through its release to water under acid conditions (see Section 3.4 above). Cr concentrations are mostly related to Fe concentration, as expected, though there are several samples which are high and do not fit this relationship. Similarly there are several, sporadic U and Se (selenium) concentrations which are higher than normal and for which a geochemical relationship is not known.

3.7. Rapid Assessment Survey

Thirteen sites were sampled for rapid acid sulfate soil assessment in July 2008. The distributions of these sites are shown in Figure 1-1 (black circles). All 13 sites indicted the presence of sulfuric or hypersulfidic materials (Appendix 1) and based on these results indicated a high potential for acidification. As a result a more detailed study was actioned and this report describes the detailed study and findings.

4. GOOLWA CHANNEL

Results from the data are provided under the following sub-headings. A summary of the key findings are listed here.

SUMMARY

The Goolwa Channel soils tend to have sandy surface soils that progressively become clayey with trans-horizon polygonal desiccation cracks, which often form large columnar structures.

The hypersulfidic material tends to be associated with the black (or dark grey), soft, clay subsoil.

Significant quantities of schwertmannite, sideronatrite, jarosite, natrojarosite and sulfate-rich soluble salts (e.g. hexahydrite, epsomite, tamarugite and alunogen) that crystallise in micron thick layers on the exposed dry soil surfaces of sulfuric materials. The salts are more prominent where there is clayey columnar structured soils.

pH_w values indicated that 9 of 36 samples (25% of total), from 6 out of 9 soil profiles were below the critical pH_w 4.0 value, characterising acid sulfate soil materials as sulfuric material, and all occurred within 30cm of the soil surface.

pH_{FOX} and $pH_{incubation}$ values indicated about 45% of samples could realistically be expected to acidify below pH 4.0 on exposure to air (oxygen) under moist conditions. Hence, most samples classify as hypersulfidic and these materials were found in all 15 profiles.

The Net Acidity values ranged from 2575 to -2277 moles H^+/tonne, and 19 of 36 soil samples analysed were positive. This indicates that 53% of soil samples either contain existing acidity and / or have the potential to further produce acid as they oxidise.

4.1. Site and Soil Characteristics – Goolwa Channel

The Goolwa Channel area had 9 soil profiles described and sampled. The site positions are shown in Figure 1-1, co-ordinates and site description are presented in Table 3-1, and profile descriptions in Appendix 3. Two separate transect locations characterised both the western side of the channel (CUR11 to 14) and north-eastern side (CUR15 to 19).

The two transects have been drawn up as conceptual toposequence models (Figure 4-1, Figure 4-2) that show a generalised relationship between the soil profiles sampled and described, and how the underlying layers and acid sulfate soil materials vary in the landscape.

Toposequence CUR11 to 14 (Figure 4-1) transect is characterised by a loose sandy surface near the land side which progressively becomes loamy then clayey as it nears the water towards the Goolwa channel. Mid way along (e.g. CUR 13) where the surface is dry there is prominent surface cracking forming columns that have substantial orange-coloured coatings of schwertmannite (pH ranging between 3 to 3.6), and within these soil materials between a depth of 30 to 60 cm are light yellow or straw coloured mottles comprising mainly natrojarosite and jarosite mottles, which surround old Phragmites root channels in a dark grey matrix. Underlying this sulfuric material is black, very soft, clay that classifies as hypersulfidic material. In the shallow water where the clay layer is exposed under the water there are soil cracks that contain monosulfidic material.

The conceptual toposequence model for the CUR15 to 19 (Figure 4-2) transect is characterised by a firm brownish grey sandy surface that has some areas forming pockets of black fibrous organic material (e.g. CUR 17). Underlying is sandy clay that overlies yellowish clay that contains parts of a calcrete layer (e.g. CUR 18). The sandy dry surface near the land side has prominent thin layers of sideronatrite on the surface, and mid-way along the toposequence transect there is sulfuric material with prominent mottles and streaks with natrojarosite and in the upper soil layers (e.g. CUR 18). The lower dark grey layers all contain hypersulfidic materials.

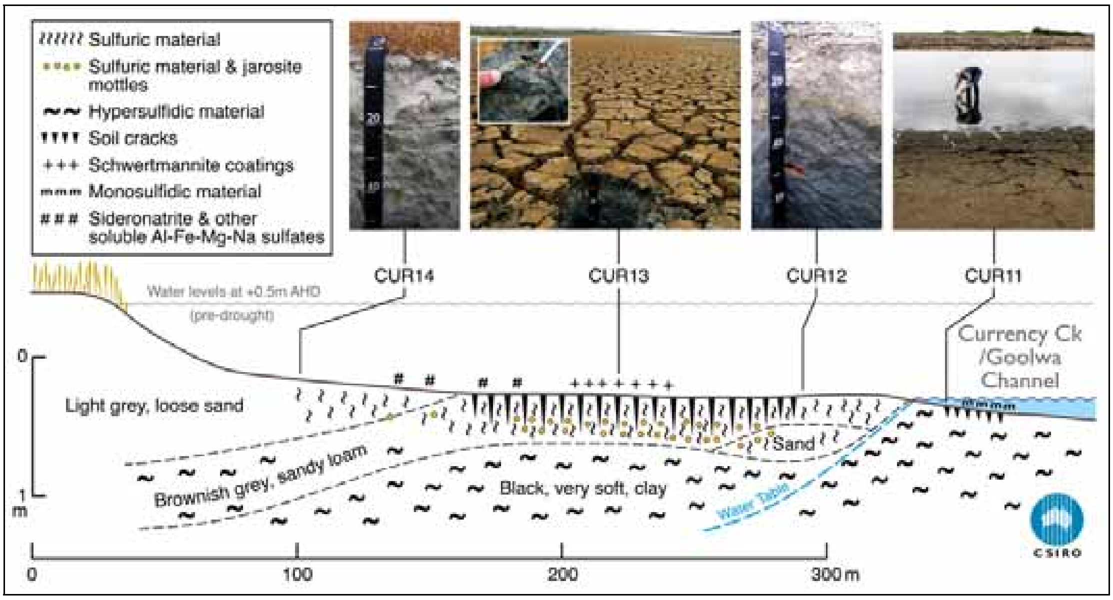


Figure 4-1: Conceptual toposequence model for Sites CUR11 to 14, located on the western side of Goolwa Channel / Currency Creek.

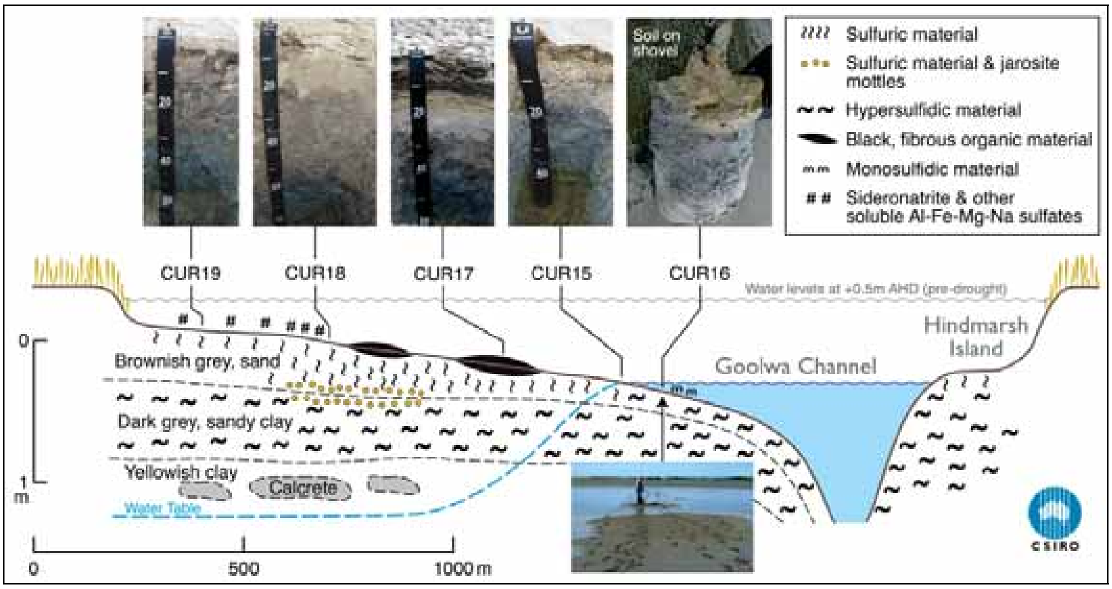


Figure 4-2: Conceptual toposequence model for Sites CUR15 to 19, located on the north-eastern side of Goolwa Channel / Currency Creek.

4.2. Acid Generating Potential – Goolwa Channel

4.2.1. Soil pH testing (pH_W, pH_{FOX} and $pH_{incubation}$)

Soil pH data for 36 soil samples from 9 soil profile sites measured in the Goolwa Channel area are listed in Appendix 4. These values are presented below as pH depth plots and the sites have been grouped according to the sampling transects that they came from (Figure 4-3, Figure 4-4).

The pH_w values ranged from 2.6 (CUR18 20-50 cm) to 8.6 (CUR18 75-90 cm). Nine samples from 6 soil profiles had a pH_w that was below the critical pH_w 4.0 value, 25% of soil samples, characterising the soil sample as sulfuric material, and all occurred within 30cm of the soil surface.

Following treatment with peroxide the soil pH dropped significantly and pH_{FOX} values ranged from 1.5 (CUR17 27-40 cm) to 7.6 (CUR15 40-60 cm). Sixteen samples from 9 soil profiles were below the critical pH_{FOX} value of 2.5, 44% of soil samples, which indicates the soil is likely to have the potential to acidify to less than 4 on exposure to air (oxygen) under moist conditions.

Chip-tray soil samples were incubated and measured for pH at 11 and 20 weeks. The 20 week pH values are presented in the figures and the 11 week pH values are listed in Appendix 4. The 20 week $pH_{incubation}$ values ranged from 1.9 (CUR17 40-48 cm) to 7.0 (CUR15 40-60 cm). Seventeen samples from 7 soil profiles dropped to below pH 4.0, 47% of samples, indicating a more realistic scenario with regard to what will happen during rewetting of the soils. All but 4 of these 17 samples occurred within 30 cm of the soil surface.

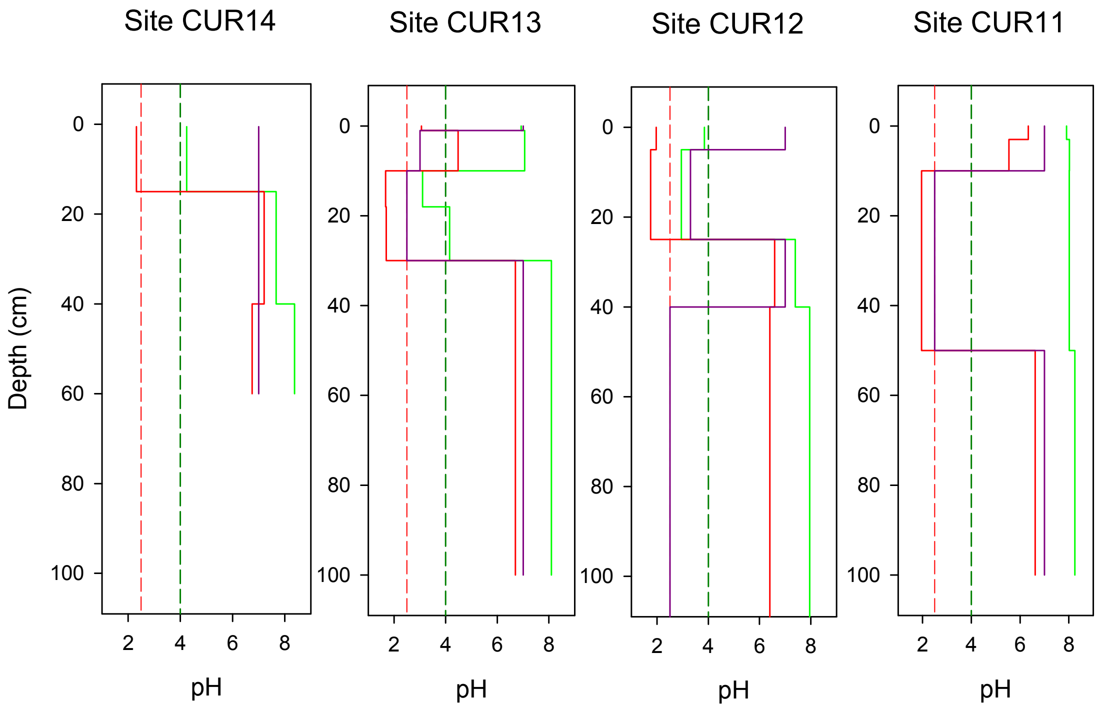


Figure 4-3: Depth profiles of pH for transect CUR11 to 14, showing soil pH (pH_w as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_w and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from land to water.

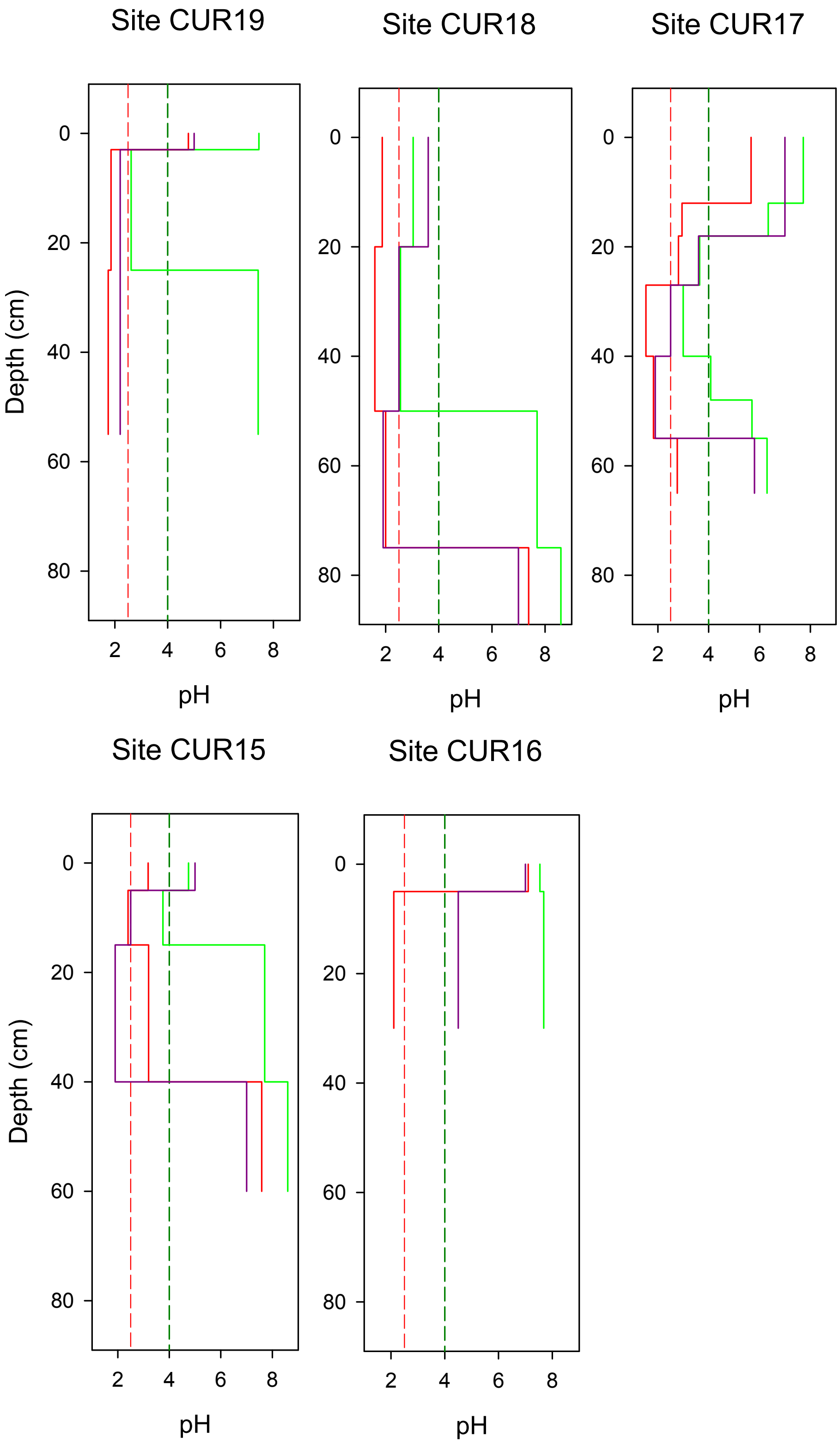


Figure 4-4: Depth profiles of pH for transect CUR15-19, showing soil pH (pH_w as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_w and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from land to water.

4.2.2. Sulfur chemistry and acid-base accounting

Acid-base accounting data for 36 soil samples from 9 soil profiles were measured in the Goolwa Channel area, and are listed in Appendix 5. These values are presented below as Net Acidity plots and plots showing the components of the Net Acidity, the sites have been grouped according to the sampling transects that they came from (Figure 4-5, Figure 4-6).

There were 15 samples that had a pH_{KCl} below 6.5, indicating they contain Existing Acidity as TAA. Where measurements of pH_{KCl} are below 6.5, by definition ANC is considered to be zero.

The Net Acidity values ranged from 2,575 to -2,277 moles H^+/tonne, and 19 of 36 soil samples analysed were positive, indicating that 53% of soil samples either contain Existing Acidity and / or have the potential to further produce acid as they oxidise.

Water extractable sulfate values are very high with all samples having greater than 100 mg SO_4 /kg of soil.

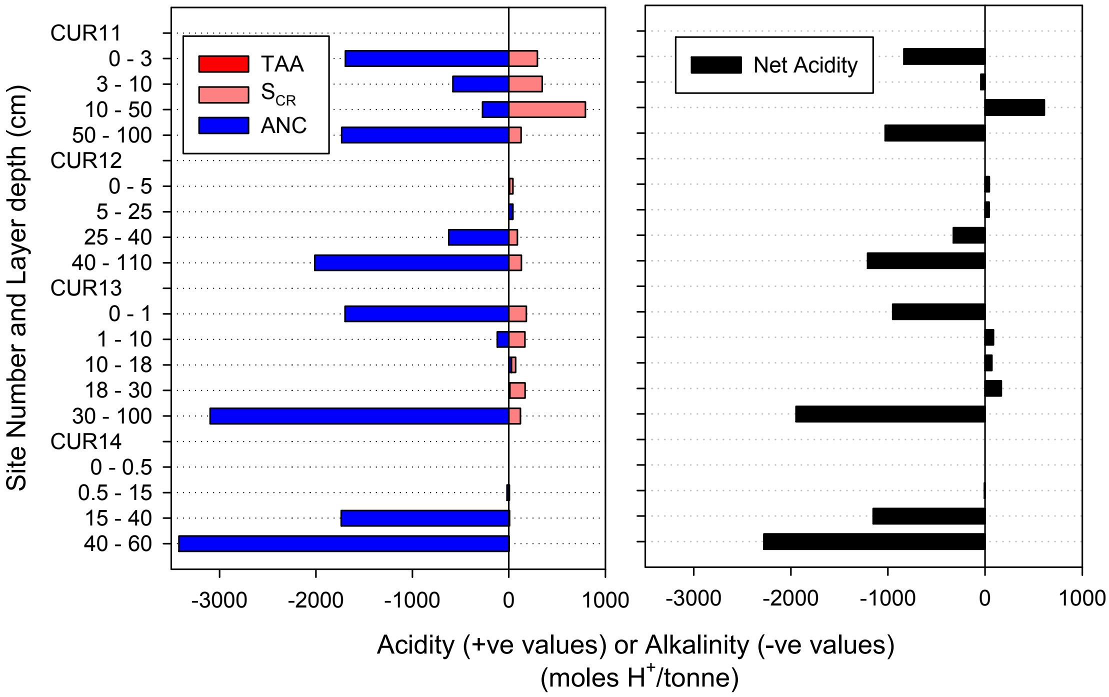


Figure 4-5: Net Acidity (NA) depth profiles for transect CUR11-14. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

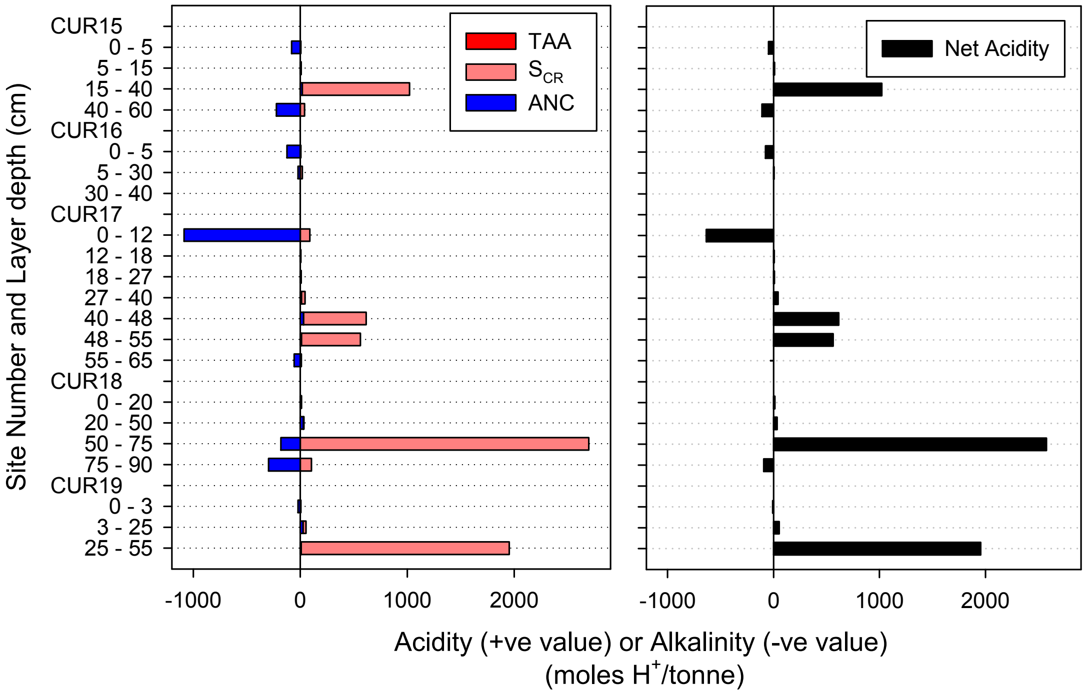


Figure 4-6: Net Acidity (NA) depth profiles for transect CUR15-19. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

5. CURRENCY CREEK

Results from the data are provided under the following sub-headings. A summary of the key findings are listed here.

SUMMARY

The toposequence conceptual models for transects in Currency Creek are characterised by soil surfaces that are firm and sandy and in some areas deep cracks had formed to create a columnar structure.

Hypersulfidic material tends to be associated with the black (or dark grey), soft, clay subsoil.

Prominent yellowish and orange patches occur on the surface where significant quantities of sideronatrite and schwertmannite occur on the dry soil surfaces, and with jarosite at depth (5 to 30 cm) especially where there is clayey columnar structured soils.

The pH_w values indicated that 10 of 24 samples (42% of total), from 4 out of 7 soil profiles were below the critical value of 4.0, characterising the soil sample as sulfuric material, and all occurred within 30cm of the soil surface.

The pH_{FOX} and $pH_{incubation}$ values indicated about 75% of samples could realistically be expected to acidify to below 4.0 on exposure to air (oxygen) under moist conditions. Characterising the soil samples as hypersulfidic and these materials were found in all 7 profiles. Thick layers (0 to 30 cm) of monosulfidic material was found below algal mats in Currency Creek.

The Net Acidity values ranged from 976 to -40 moles H^+/tonne, and 21 of 24 soil samples analysed were positive. Indicating that 88% of soil samples either contain existing acidity and / or have the potential to further produce acid as they oxidise.

5.1. Site and Soil Characteristics – Currency Creek

Currency Creek area had 9 soil profiles described and sampled. The site positions are shown in Figure 1-1, co-ordinates and site description are presented in Table 3-1, and the profile descriptions are presented in Appendix 3. Two separate transect locations characterised both the upper northern side of the Creek (CUR20 to 25) and middle north-eastern side (CUR26 to 28).

One of the transects has been developed as a conceptual toposequence model (Figure 5-1) to show a generalised relationship between the soil profiles sampled and described and how the underlying layers and acid sulfate soil materials vary across the landscape.

Toposequence CUR27 to 28 (Figure 5-1) transect is characterised by sandy surface materials to a depth of 50 cm. The widespread occurrences of bright yellowish, 2 to 5 mm thick, sandy friable crusts can be observed in CUR28. These layers contain mainly precipitates of the mineral sideronatrite, which occur as rosettes and platelets (Fitzpatrick and Shand 2008) within sulfuric material (< pH 2.5) on the soil surface. Sideronatrite is derived from the oxidation and dissolution of pyrite framboids, which occur mainly in the form of spheroidal aggregates of pyrite crystals. Sideronatrite in the yellowish crusts dissolves and re-precipitates as orange coloured schwertmannite (CUR 27) in immediately adjacent zones where the pH is slightly less acidic, to display distinct orange patches or areas on the soil surface and orange mottles to a depth of 2 to 10 cm (CUR 27). This mineral forming process occurs during rainfall cyclic wetting and drying events, which causes water to dissolve sideronatrite and transport ferrous Fe and sulfate ions to adjacent “micro-ponds” where schwertmannite rapidly crystallises (Fitzpatrick and Shand 2008). The formation of these minerals is indicative of local geochemical environments that are rapidly changing with variations in pH and rates of Fe, S and Na mineralisation.

Finally, thick layers (0 to 30 cm) of monosulfidic material occur below thin algal mats in the subaqueous acid sulfate soil soils in Currency Creek (e.g. CUR 26).

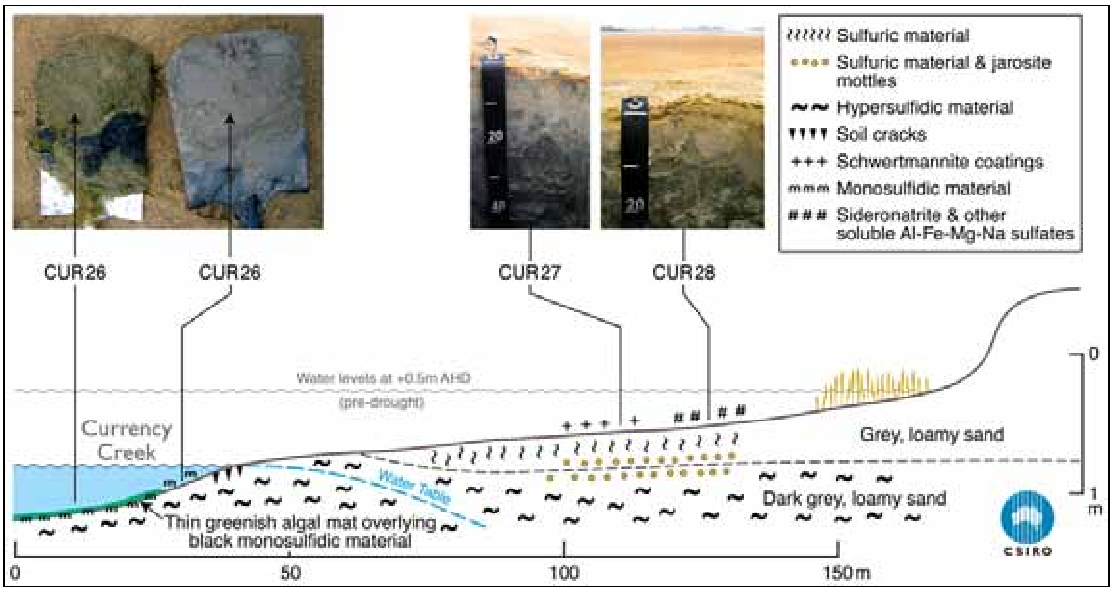


Figure 5-1: Conceptual toposequence model for Sites CUR27 to 28, located on the north-eastern side of Currency Creek.

5.2. Acid Generating Potential – Currency Creek

5.2.1. Soil pH testing (pH_W, pH_{FOX} and $pH_{incubation}$)

Soil pH data for 24 soil samples from 7 soil profile sites measured in the Currency Creek area are listed in Appendix 4. These values are presented below as pH depth plots, and the sites have been grouped according to the sampling transects that they came from (Figure 5-2, Figure 5-3, Figure 5-4).

The pH_w values ranged from 2.90 (CUR27 0.5-10 cm) to 8.3 (CUR26 0-5 cm). Ten samples from 4 soil profiles had a pH_w below the critical value of 4.0, 42% of soil samples, which characterised them as sulfuric material. All occurred within 30cm of the soil surface.

Following treatment with peroxide the soil pH dropped significantly and pH_{FOX} values ranged from 1.4 (CUR25 10-25 cm) to 5.3 (CUR27 0-0.5 cm). Twenty one samples from 7 soil profiles were below the critical pH_{FOX} value of 2.5, 88% of soil samples, which indicates the soil may have the potential to acidify to less than 4 on exposure to air (oxygen) under moist conditions.

Chip-tray soil samples were aged and measured for pH at 11 and 20 weeks. The 20 week pH values are presented in the figures and the 11 week pH values are listed in Appendix 4. The 20 week $pH_{incubation}$ values ranged from 1.6 (CUR21 25-70 cm) to 7.0 (CUR27 0-0.5 cm). Eighteen samples from seven soil profiles 75% of samples, dropped to $pH_{incubation}$ below 4.0, indicating a more realistic scenario with regard to what will happen during rewetting of these soils. All but 2 of these 18 samples occurred within 30 cm of the soil surface.

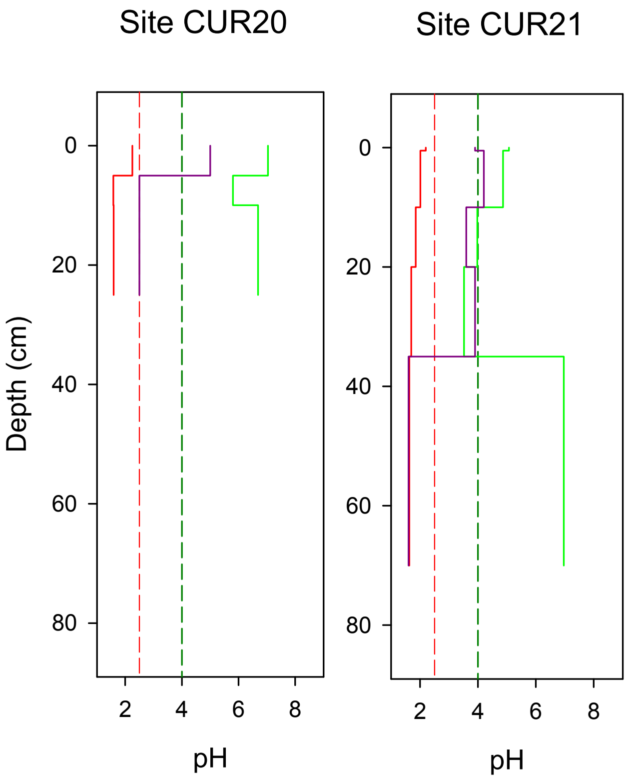


Figure 5-2: Depth profiles of pH for transect CUR20 to 21, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from land to water.

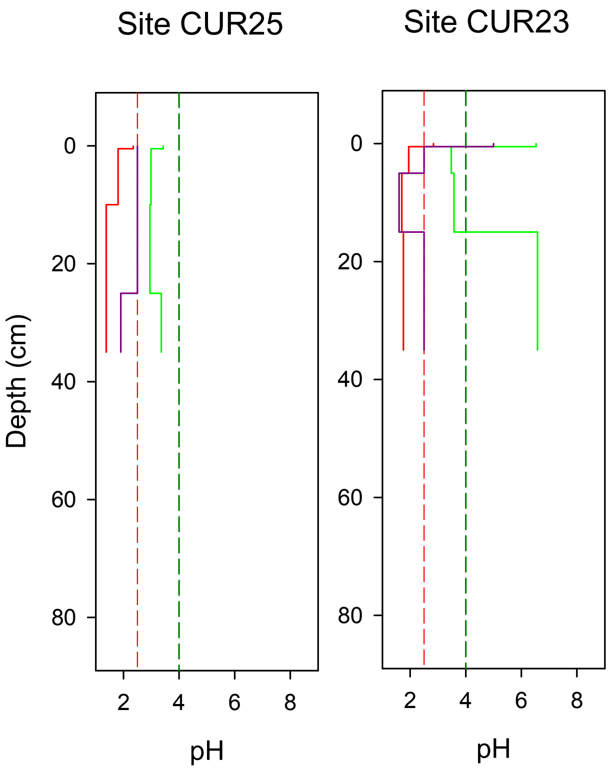


Figure 5-3: Depth profiles of pH for transect CUR23 to 25, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from land to water.

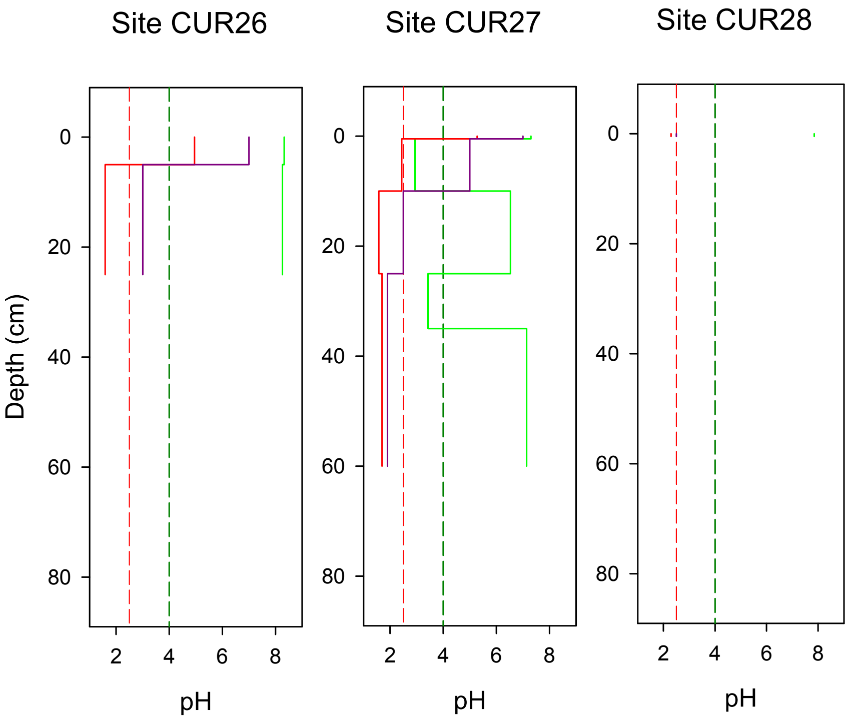


Figure 5-4: Depth profiles for transect CUR26 to 28, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from land to water.

Note Site 28 has no soil data as this was for a water sample measurement

5.2.2. Sulfur chemistry and acid-base accounting

Acid-base accounting data for 24 soil samples from 7 soil profiles were measured in the Currency Creek area are listed in Appendix 5. These values are presented below as Net Acidity plots and plots showing the components of the Net Acidity. The sites have been grouped according to the sampling transects that they came from (Figure 5-5, Figure 5-6, Figure 5-7).

There were 20 samples that had a pH_{KCl} below 6.5, indicating they contain Existing Acidity as TAA. Where measurements of pH_{KCl} are below 6.5, by definition ANC is considered to be zero.

The Net Acidity values ranged from 976 to -40 moles H^+/tonne, and 21 of 24 soil samples analysed were positive. This indicates that most, 88% of soil samples either contain Existing Acidity and / or have the potential to further produce acid as they oxidise.

Water extractable sulfate values are very high with all samples having greater than 100 mg SO_4 /kg of soil.

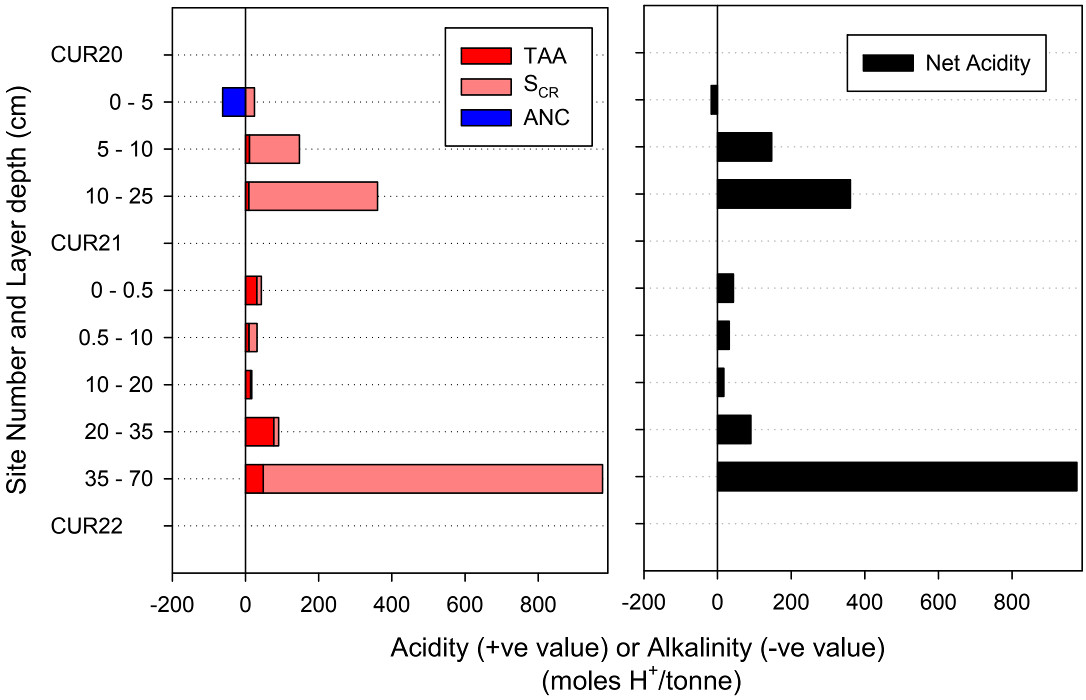


Figure 5-5: Net Acidity (NA) depth profiles for transect CUR20-22. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

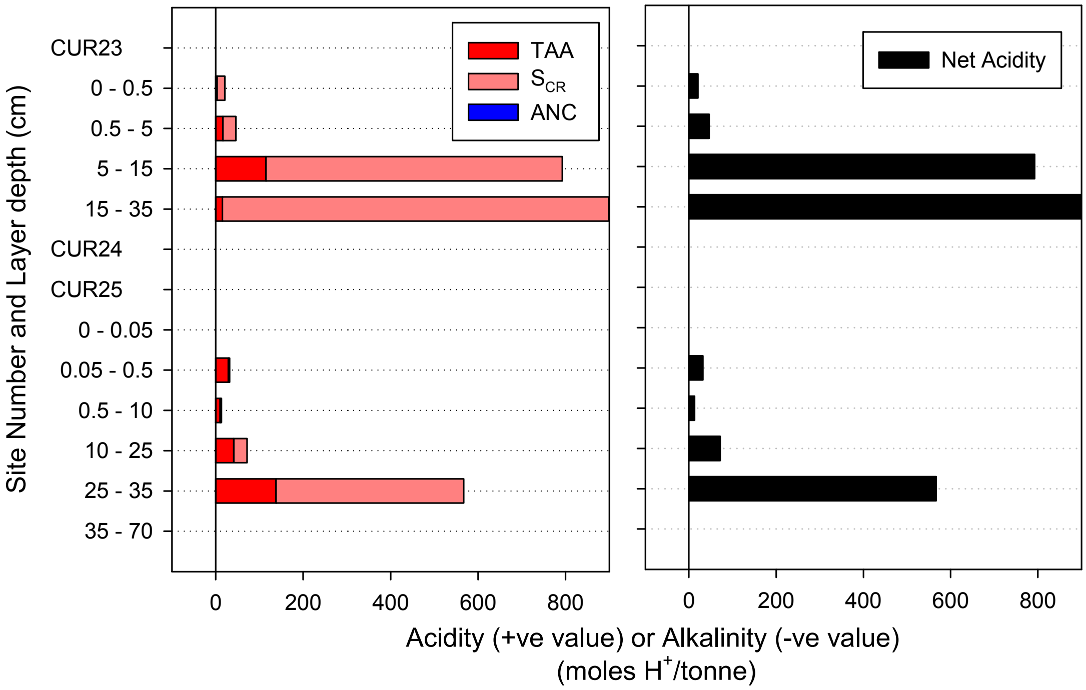


Figure 5-6: Net Acidity (NA) depth profiles for transect CUR23-25. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

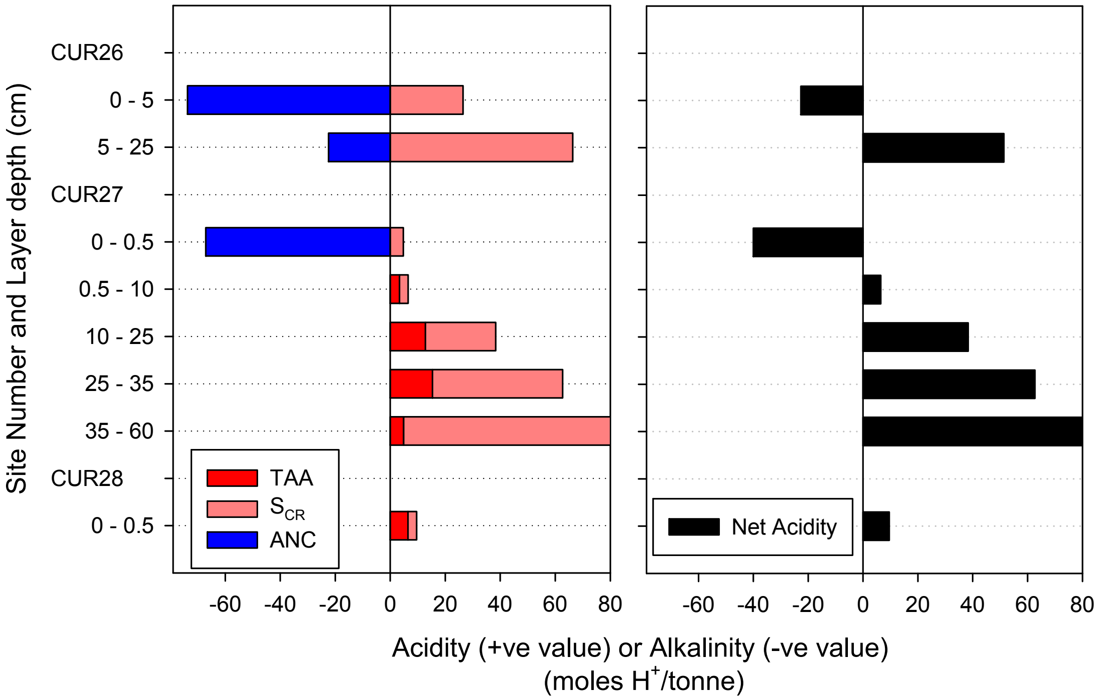


Figure 5-7: Net Acidity (NA) depth profiles for transect CUR26-28. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

6. FINNISS RIVER

Results from the data are provided under the following sub-headings. A summary of the key findings are listed here.

SUMMARY

The east side of Finniss River tends to have sandy soils whereas the west side are clayey with deep desiccation cracks forming large columnar structures.

Hypersulfidic material tends to be associated with the black (or dark grey), soft, clay subsoil.

Significant quantities of schwertmannite, sideronatrite and jarosite are observed on the dry soil surfaces, and are more prominent on the west side of Finniss River where there is clayey columnar structured soils.

The pH_w values indicated that 19 of 54 samples (35% of total), from 7 out of 15 soil profiles where below the critical 4.0 value, characterising the soil sample as sulfuric material, and all occurred within 30cm of the soil surface.

The pH_{FOX} and $pH_{incubation}$ values indicated about 70% of samples could realistically be expected to acidify below 4.0 on exposure to air (oxygen) under moist conditions, characterising the soil samples as hypersulfidic. These materials were found in all 15 profiles.

The Net Acidity values ranged from 1088 to -2077 moles H^+/tonne, and 45 of 54 soil samples analysed were positive, indicating that 83% of soil samples either contain existing acidity and / or have the potential to further produce acid as they oxidise.

6.1. Site and Soil Characteristics – Finniss River

Finniss River area had 18 soil profiles described and sampled, the site positions are shown in Figure 1-1, co-ordinates and site description are presented in Table 3-1, and profile descriptions in Appendix 3. Five separate transect locations characterised both the east (FIN20 to 25, FIN27 to 28) and west sides of the river (FIN30 to 32, FIN33 to 36, FiN37 to 39), and one location Wally's Landing (Fin26) was visited multiple times on different dates and is discussed in several sub-sections below (e.g. Section 6.2) where it shows changes with time and provides an insight to monitoring. This information has also in been used in the conclusions of this report to construct a series of "predictive" conceptual models, comprising several cross-sections to explain sequential changes with time (i.e. before the 1880s, 1880s to 1930s, 2006 to 2009 period when drying occurred due to the drought and finally during May 2009 during a rewetting period from winter rains).

Three of the transects have been drawn up as conceptual toposequences (Figure 6-1, Figure 6-2, Figure 6-3) that show a generalised relationship between the soil profiles sampled and described and how the underlying layers and acid sulfate soil materials vary across the landscape.

Toposequence FIN20 to 25 (Figure 6-1) transect is characterised by large cracks to the underlying subsoil that form columns during the drying. The top surface of the columns are extremely hard and coating the upper and side surfaces of the columns are various minerals including jarosite (FIN 20), schwertmannite (FIN 23), sideronatrite (FIN 23) and other soluble Al-Fe-Mg-Na sulfates. These clay columns overly a black soft organic rich clay layer that varies in thickness and proximity to the surface. Underlying this is a black, very soft clay. The upper columnar layer is classified as sulfuric material and the underlying soft clay as hypersulfidic material. When these acid sulfate soil materials were sampled in November 2008, the sulfuric material in the cracking clay (FIN 20) had thick soft layers (pale yellow mottles/ precipitates) of jarosite in the cracks (pH 3.3) and the water in the large cracks had a pH of 3.54 (Fitzpatrick *et al*. 2009a).

Toposequence FIN30 to 32 (Figure 6-2) transect is characterised by the sandy crusted surface. The soil profiles are sandy throughout, with a massive structure and with depth colour changes from a brown, to dark grey to black. The upper brown sand is sulfuric material and the grey and particularly black sand is sulfidic.

Toposequence FIN33 to 36 (Figure 6-3) transect is characterised by a soft sand overlying a sandy clay loam that is firm when dry and very soft when wet nearer the river. Underlying is very soft clay. Where the surface is dry coatings of schwertmannite and sideronatrite occur. There is a thin sulfuric material layer at the surface and underlying is sulfidic material

Toposequence FIN37 to 39 transect is not shown as a diagram but is essentially the same as transect FIN33 to 36.

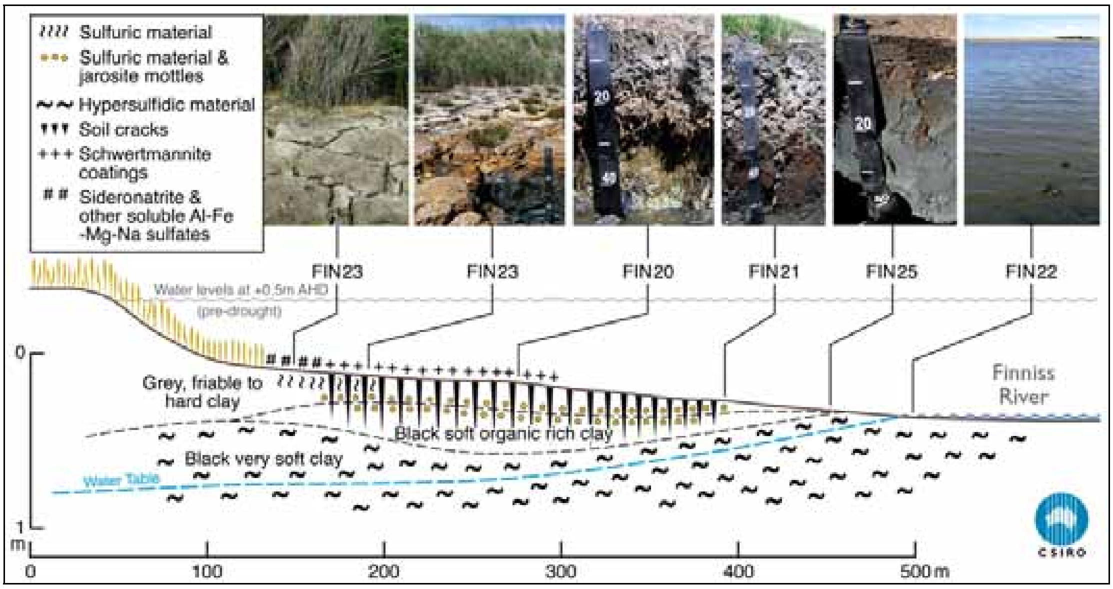


Figure 6-1: Conceptual toposequence model for Sites FIN20 to 25, located on the west side of Finniss River.

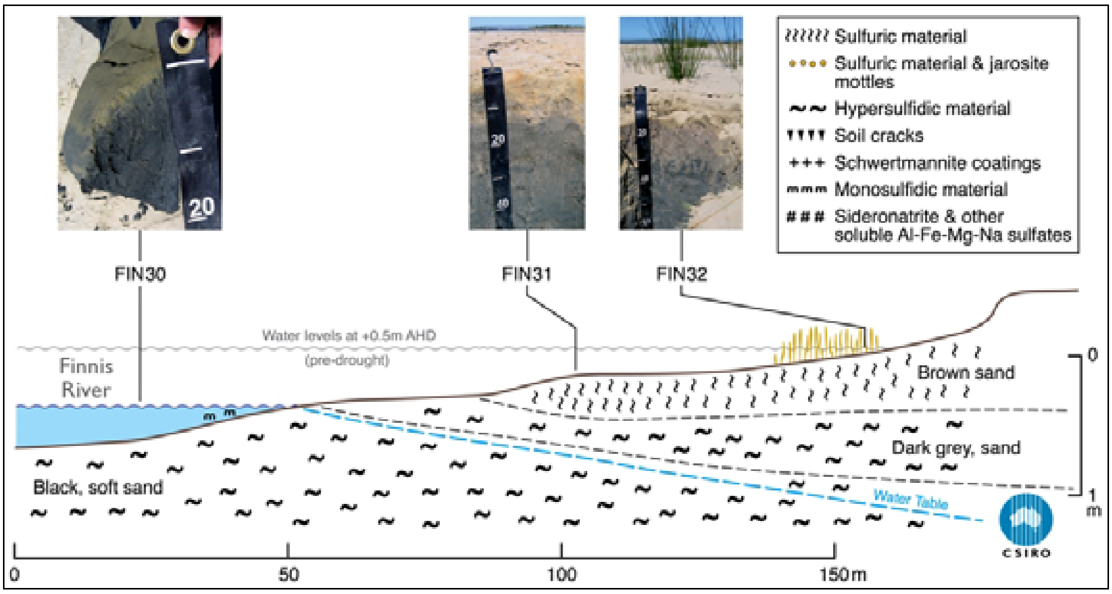


Figure 6-2: Conceptual toposequence model for Sites FIN30 to 32, located on the east side of Finniss River.

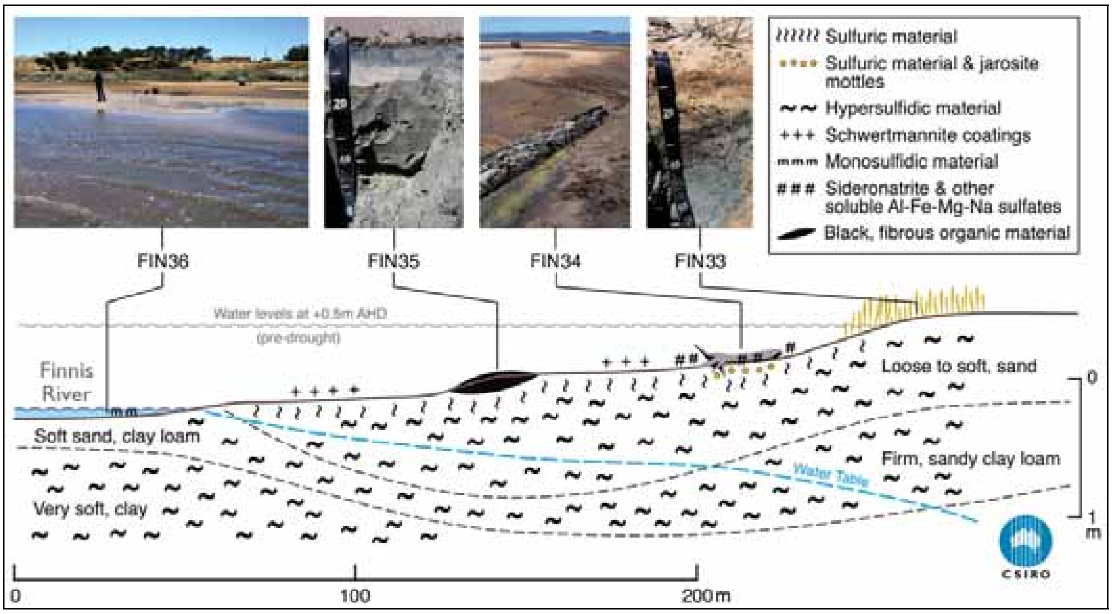
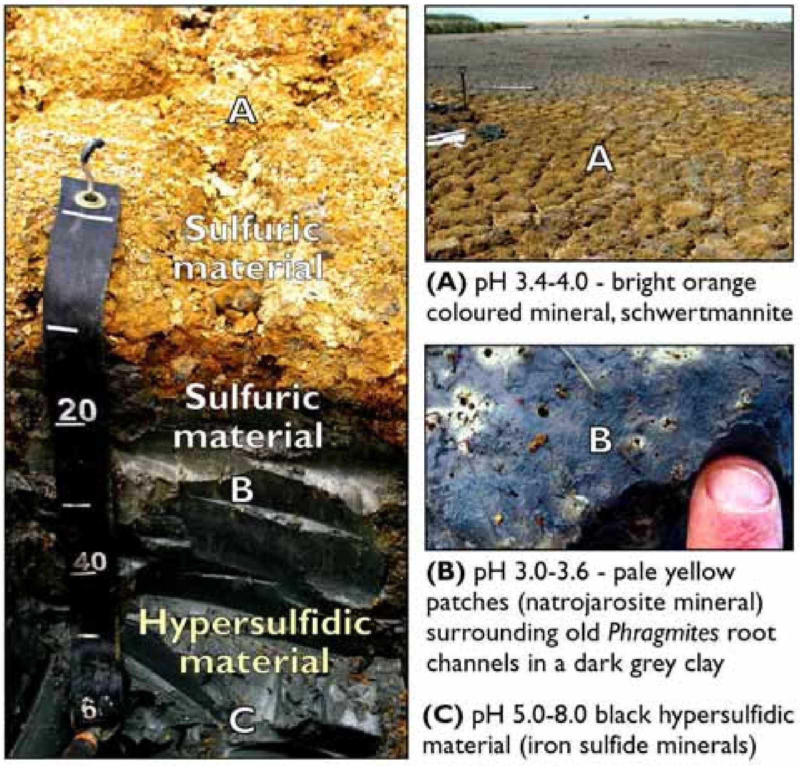


Figure 6-3: Conceptual toposequence model for Sites FIN33 to 36, located on the east side of Finniss River.

Toposequence FIN27 to 28 transect is not shown as a diagram but is essentially the same as part of transect FIN21 to 25. A typical sulfuric cracking clay soil (FIN28) in the clayey dry river-bed of the Finniss River, showing a soil pit with black hypersulfidic material (iron sulfides) at depth (> 60 cm) overlying sulfuric material, is presented in Figure 6-4. Light yellow or straw coloured mottles comprising mainly natrojarosite immediately overlies the sulfidic material between a depth of 30 to 60 cm, which in turn overlies a cracked surface layer (0 to 30 cm) with a pH ranging between 3 to 3.6 comprising mainly the bright orange mineral, schwertmannite. Pale yellow mottles (right hand side) can be seen surrounding old Phragmites root channels in a dark grey matrix (from Fitzpatrick *et al*. 2009).

Sites FIN26 is at the Wally's Landing location and discussed later in Sub-section 6.2.



(A) pH 3.4-4.0 - bright orange coloured mineral, schwertmannite

(B) pH 3.0-3.6 - pale yellow patches (natrojarosite mineral) surrounding old *Phragmites* root channels in a dark grey clay

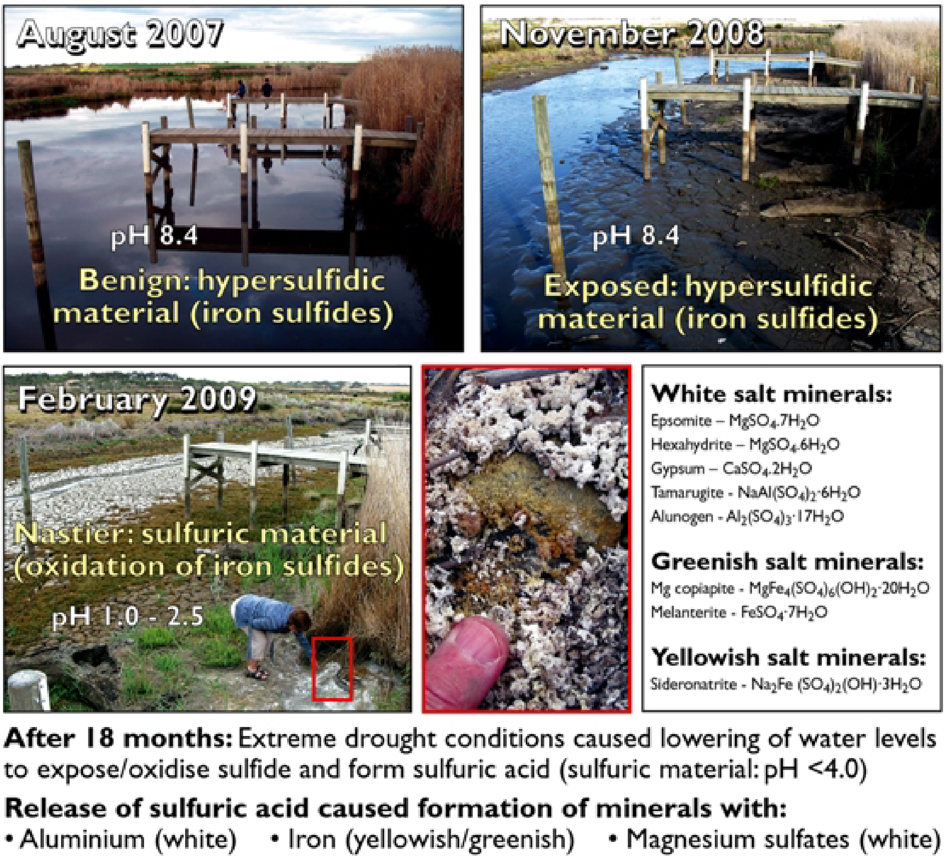
(C) pH 5.0-8.0 black hypersulfidic material (iron sulfide minerals)

Figure 6-4: A typical sulfuric cracking clay soil (FIN28) in the clayey dry river bed of the Finniss River, showing a soil pit with black hypersulfidic material (iron sulfides) at depth (>60 cm) with overlying sulfuric material.

6.2. Monitoring at Wally's Landing

Changes in water level in the Finniss River at Wally's Landing (AA26 and FIN26), which is the sampling site furthest upstream on the western side of the Finniss River (labelled as FIN 26 in Figure 1-1) are shown in photographs (Figure 6-5 and Appendix 10). The August 2007 photograph showing the whole river ponded with water. A hypersulfidic subaqueous clayey soil was sampled under 80 cm of water at the end of the jetty and labelled as sample AA26. Hypersulfidic organic clayey soil was sampled in the Phragmites four metres from the bank/waters edge and labelled as sample AA27 (see Fitzpatrick *et al*. 2008b pp. 99 and 118 for morphological and chemical data respectively). The November 2008 photograph shows substantial lowering of water levels to produce mainly waterlogged or saturated acid sulfate soil (hypersulfidic cracking clay soil – end of jetty). The February 2009 photograph shows further lowering of water levels to expose a clayey dry river-bed with cracks and salt efflorescences (sulfuric cracking clay soil). The red square in the February 2009 photograph indicates the location of the acidic white fluffy salt efflorescences adjacent to the Phragmites, which is shown in close-up on the lower right hand side photograph.

The white fluffy salt efflorescences comprises mixtures of mainly Mg-sulfate minerals [hexahydrite $MgSO_4.6H_2O$, epsomite $MgSO_4.7H_2O$] and gypsum) and bright yellowish green coloured iron oxyhydroxysulfate minerals comprising mainly sideronatrite [$Na_2Fe(SO_4)_2OH.H_2O$], tamarugite [$NaAl(SO_4)_2.6H_2O$] Mg-copiapite and melanterite with pH values of 1.6 to 2.5 overlying clayey sulfuric material (sulfuric cracking clay soil) (see Appendix 9 for XRD).



White salt minerals:
Epsomite – $MgSO_4.7H_2O$
Hexahydrite – $MgSO_4.6H_2O$
Gypsum – $CaSO_4.2H_2O$
Tamarugite - $NaAl(SO_4)_2 \cdot 6H_2O$
Alunogen - $Al_2(SO_4)_3 \cdot 17H_2O$

Greenish salt minerals:
Mg copiapite - $MgFe_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Melanterite - $FeSO_4 \cdot 7H_2O$

Yellowish salt minerals:
Sideronatrite - $Na_2Fe\ (SO_4)_2(OH) \cdot 3H_2O$

After 18 months: Extreme drought conditions caused lowering of water levels to expose/oxidise sulfide and form sulfuric acid (sulfuric material: pH <4.0)

Release of sulfuric acid caused formation of minerals with:
- Aluminium (white)
- Iron (yellowish/greenish)
- Magnesium sulfates (white)

Figure 6-5: Wally's Landing, showing change in water level at site for August 2007, November 2008 and February 2009.

6.3. Acid Generating Potential – Finniss River

6.3.1. Soil pH testing (pH_W, pH_{FOX} and $pH_{incubation}$)

Soil pH data for 54 soil samples from 15 soil profile sites were measured in the Finniss River area are listed in Appendix 4. These values are presented below as pH depth plots and the sites have been grouped according to the sampling transects that they came from (Figure 6-6, Figure 6-7, Figure 6-8, Figure 6-9, Figure 6-10).

The pH_W values ranged from pH 2.0 (FIN31 30-90 cm) to pH 8.3 (FIN25 15-70 cm). Nineteen samples from 7 soil profiles had a pH_W where below the critical 4.0 value, 35% of soil samples, characterising the soil sample as sulfuric material, and all occurred within 30cm of the soil surface.

Following treatment with peroxide the soil pH dropped significantly and pH_{FOX} values ranged from 1 (FIN20 10-18 cm) to 6.8 (FIN33 40-70 cm). Forty one samples from 15 soil profiles where below the critical pH_{FOX} value of 2.5, 76% of soil samples, which indicates the soil may have the potential to acidify to less than 4 on exposure to air (oxygen) under moist conditions.

Chip-tray soil samples were aged and measured for pH at 11 and 20 weeks. The 20 week pH values are presented in the figures and the 11 week pH values are listed in Appendix 4. The 20 week $pH_{incubation}$ values ranged from 1.3 (FIN38 30-50 cm) to 7.9 (FIN38 0-1 cm). Thirty eight samples from 15 soil profiles dropped to below 4.0, 70% of samples, indicating a more realistic scenario with regard to what will happen during rewetting of the soils. All but 5 of these 38 samples occurred within 30 cm of the soil surface.

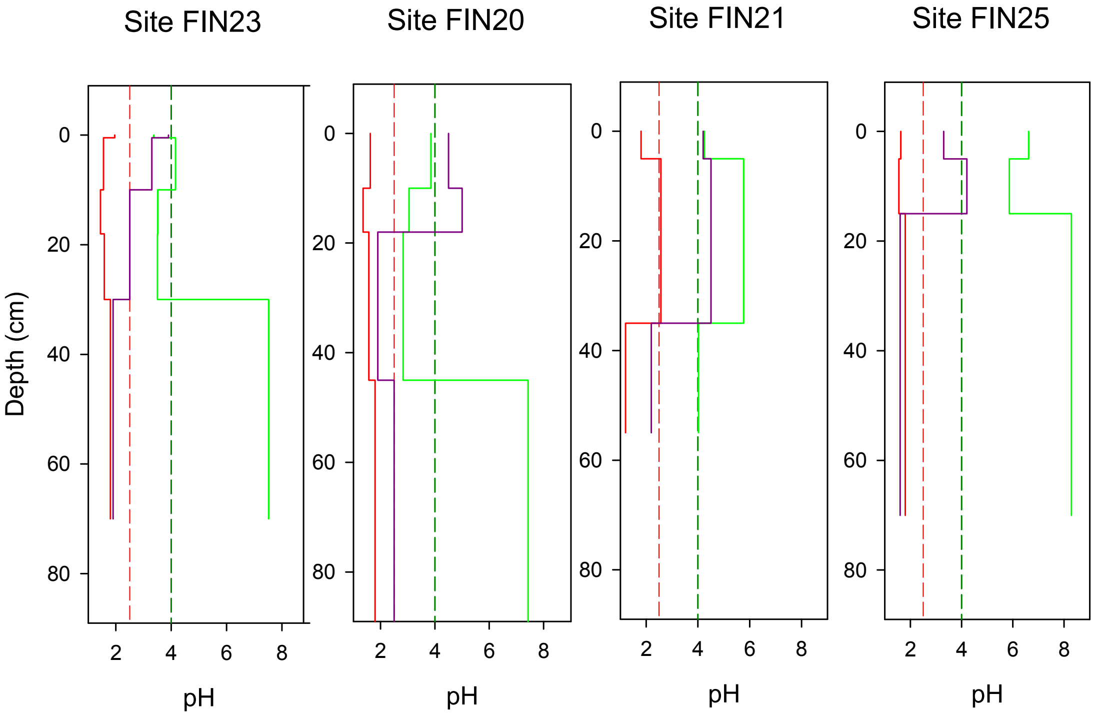


Figure 6-6: Depth profiles of pH for transect FIN20 to 25, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from land to water.

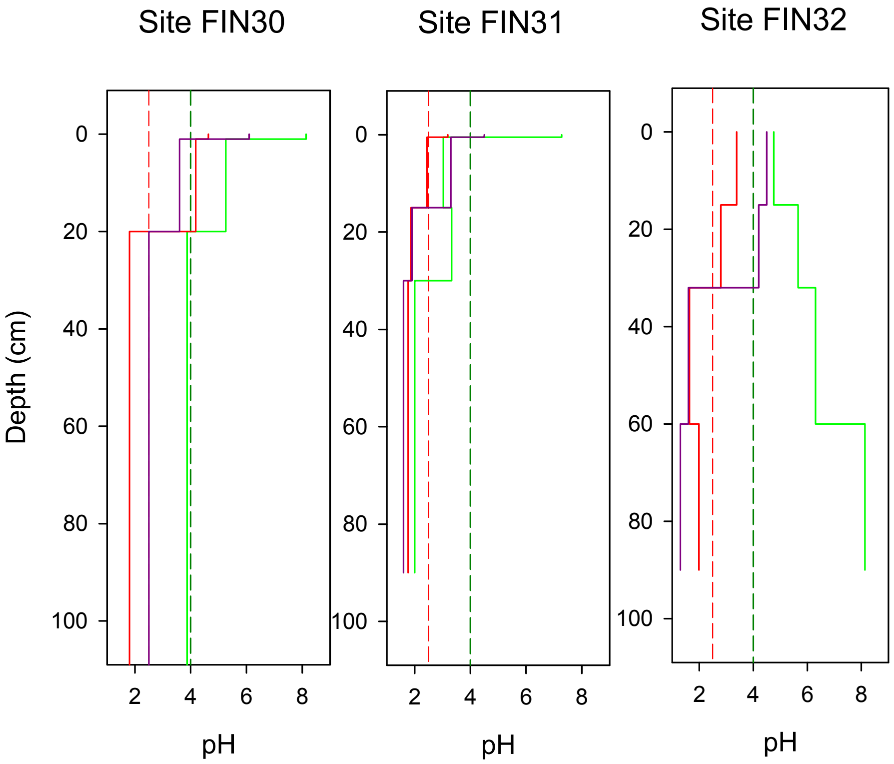


Figure 6-7: Depth profiles of pH for transect FIN30 to 32, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from water to land.

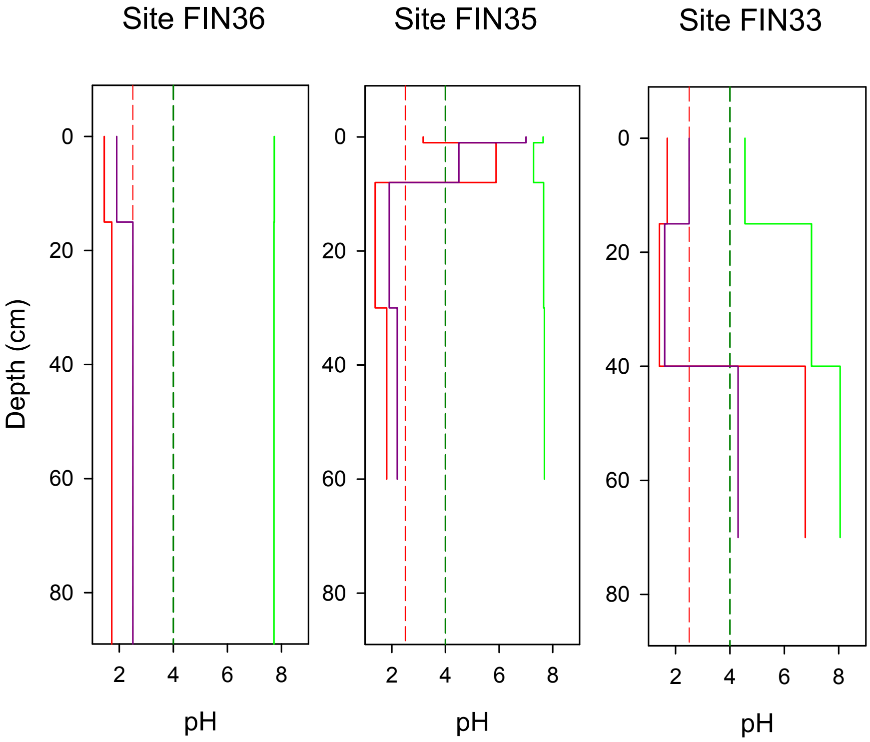


Figure 6-8: Depth profiles of pH for transect FIN33 to 36, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from water to land.

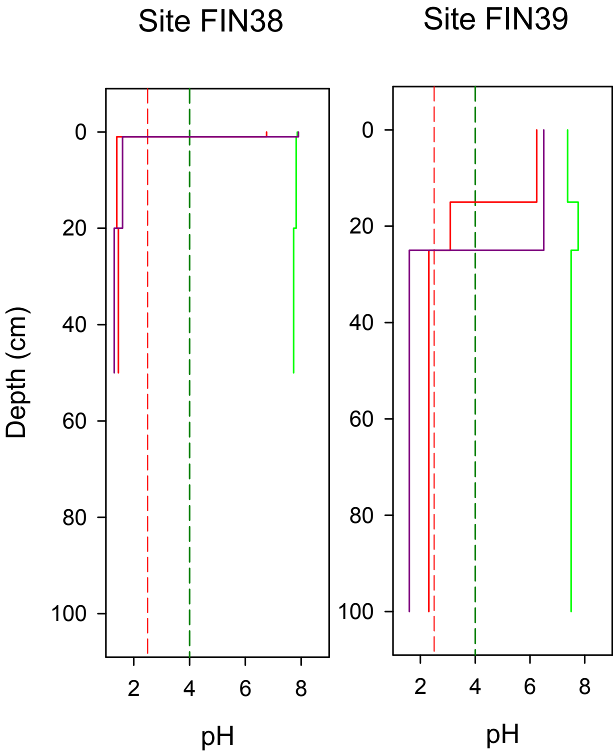


Figure 6-9: Depth profiles of pH for transect FIN37 to 39, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from water to land.

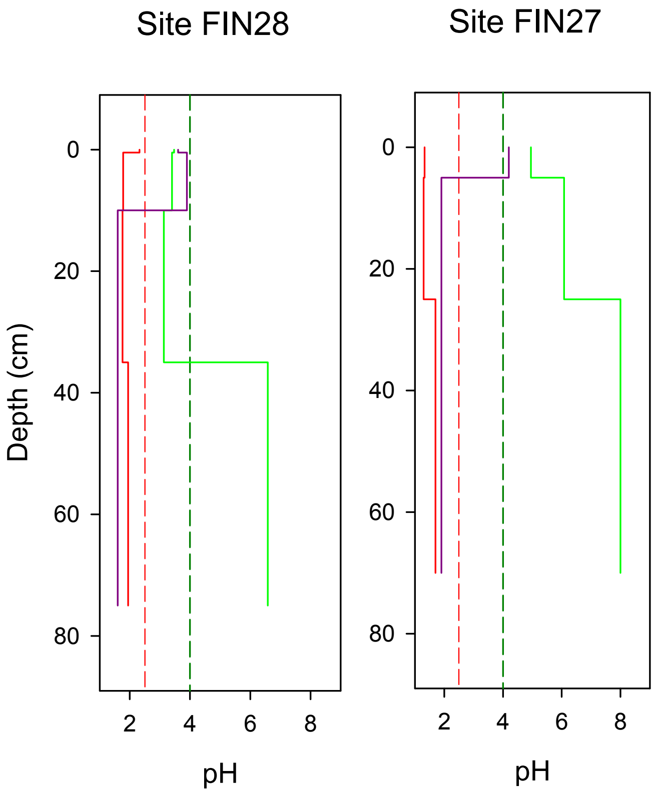


Figure 6-10: Depth profiles of pH for transect FIN27 to 28, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line). Sites are arranged according to the transect order with left to right being from land to water.

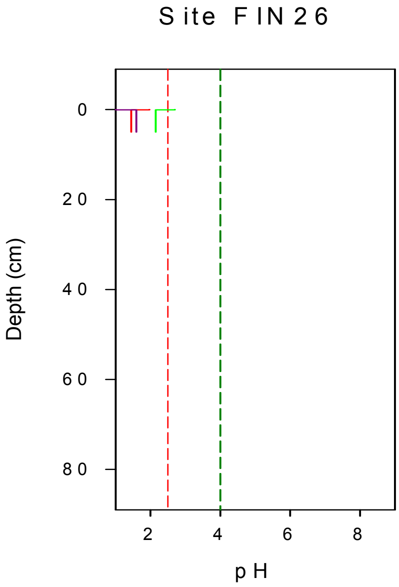


Figure 6-11: Depth profiles of pH for transect FIN26, Wally's Landing, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line).

6.3.2. Sulfur chemistry and acid-base accounting

Acid-base accounting data for 54 soil samples from 15 soil profiles were measured in the Finniss River area are listed in Appendix 5. These values are presented below as Net Acidity plots and plots showing the components of the Net Acidity, the sites have been grouped according to the sampling transects that they came from (Figure 6-13, Figure 6-14, Figure 6-15, Figure 6-16, Figure 6-17).

There were 35 samples that had a pH_{KCl} below 6.5, indicating they contain Existing Acidity as TAA. Where measurements of pH_{KCl} are below 6.5, by definition ANC is considered to be zero.

The Net Acidity values ranged from 1088 to -2077 moles H^+/tonne, and 45 of 54 soil samples analysed were positive. Indicating that most, 83% of soil samples either contain Existing Acidity and / or have the potential to further produce acid as they oxidise.

Water extractable sulfate values are very high with all samples having greater than 100 mg SO_4 /kg of soil.

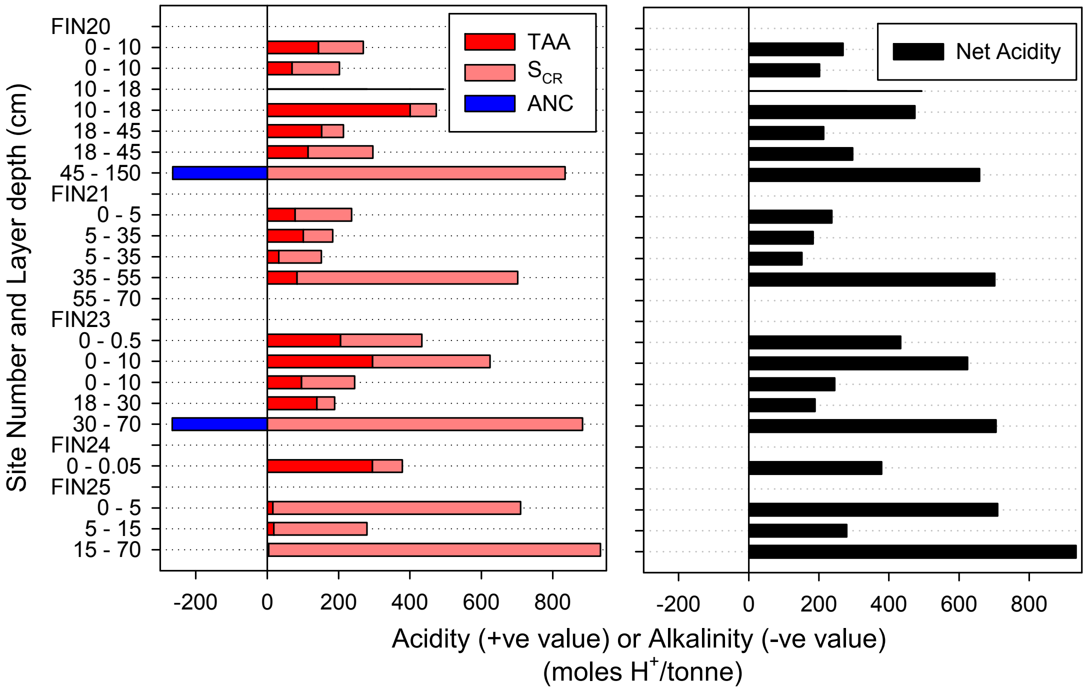


Figure 6-12: Net Acidity (NA) depth profiles for transect FIN20 to 25. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

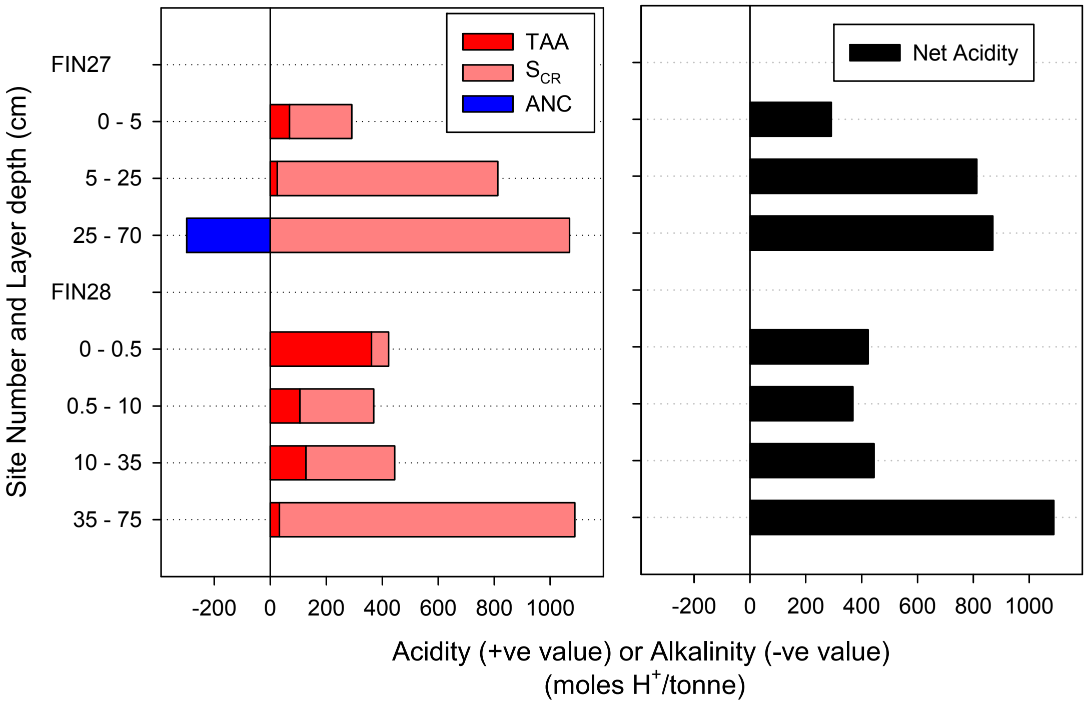


Figure 6-13: Net Acidity (NA) depth profiles for transect FIN27 to 28. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

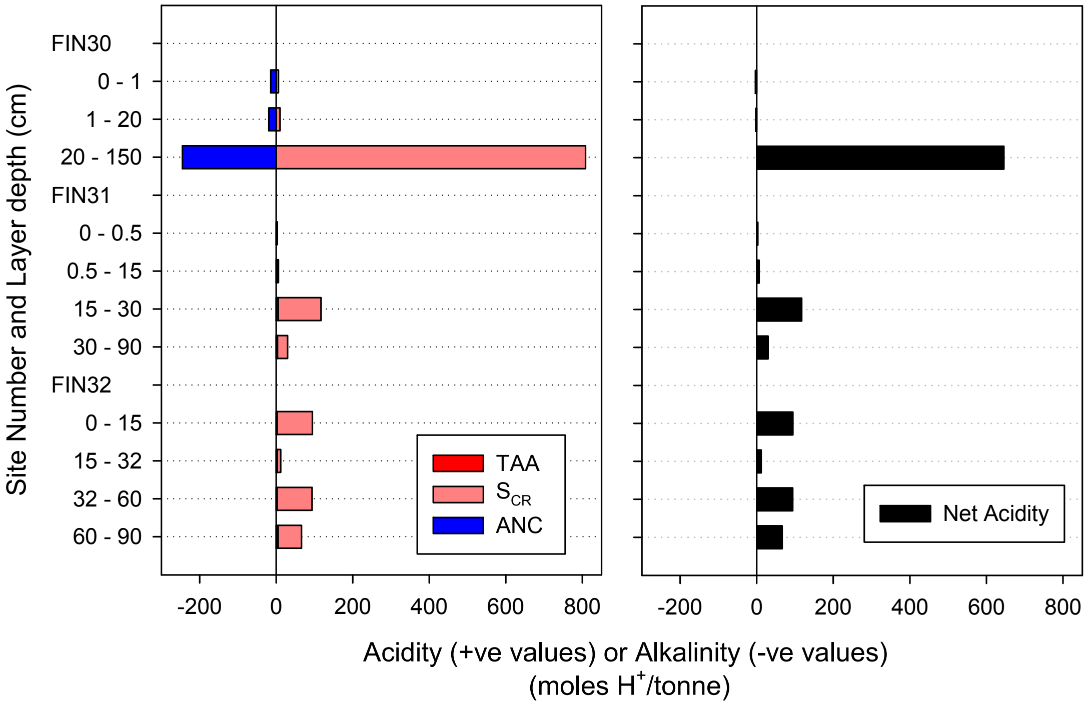


Figure 6-14: Net Acidity (NA) depth profiles for transect FIN30 to 32. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

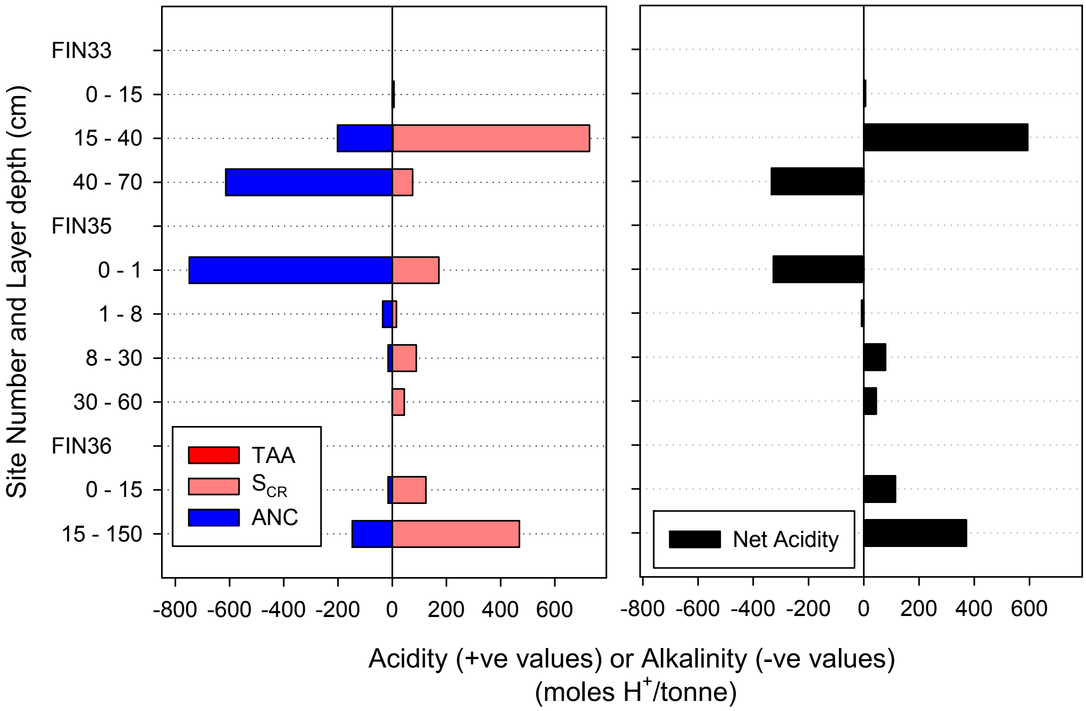


Figure 6-15: Net Acidity (NA) depth profiles for transect FIN33 to 36. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

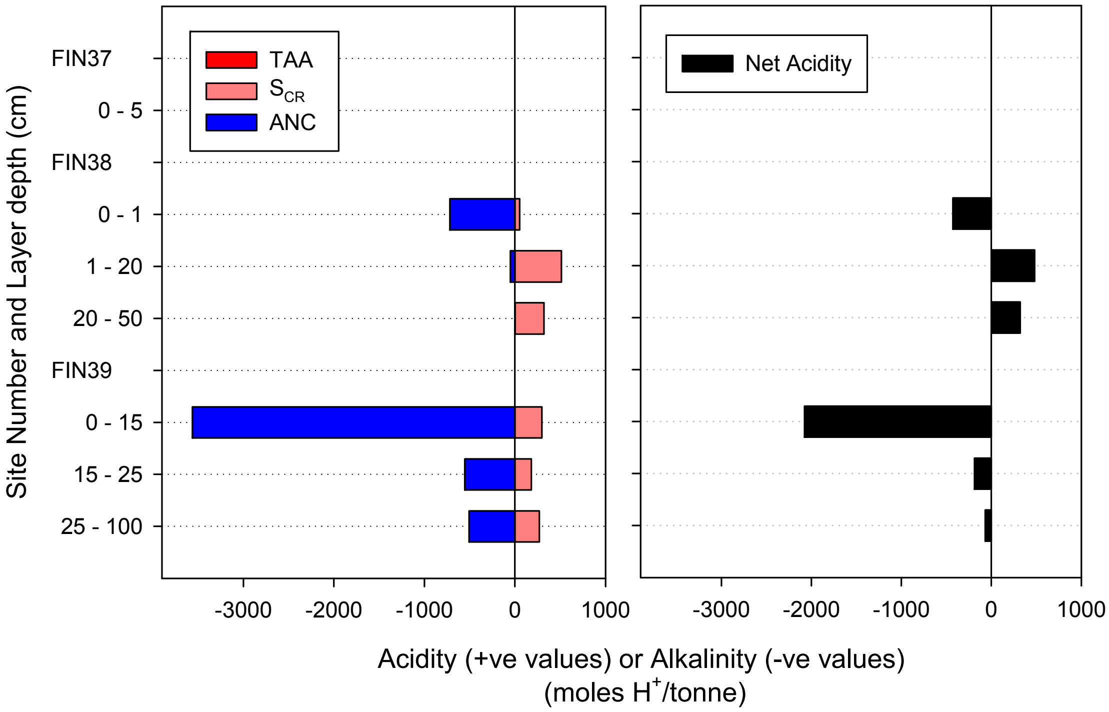


Figure 6-16: Net Acidity (NA) depth profiles for transect FIN37 to 39. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

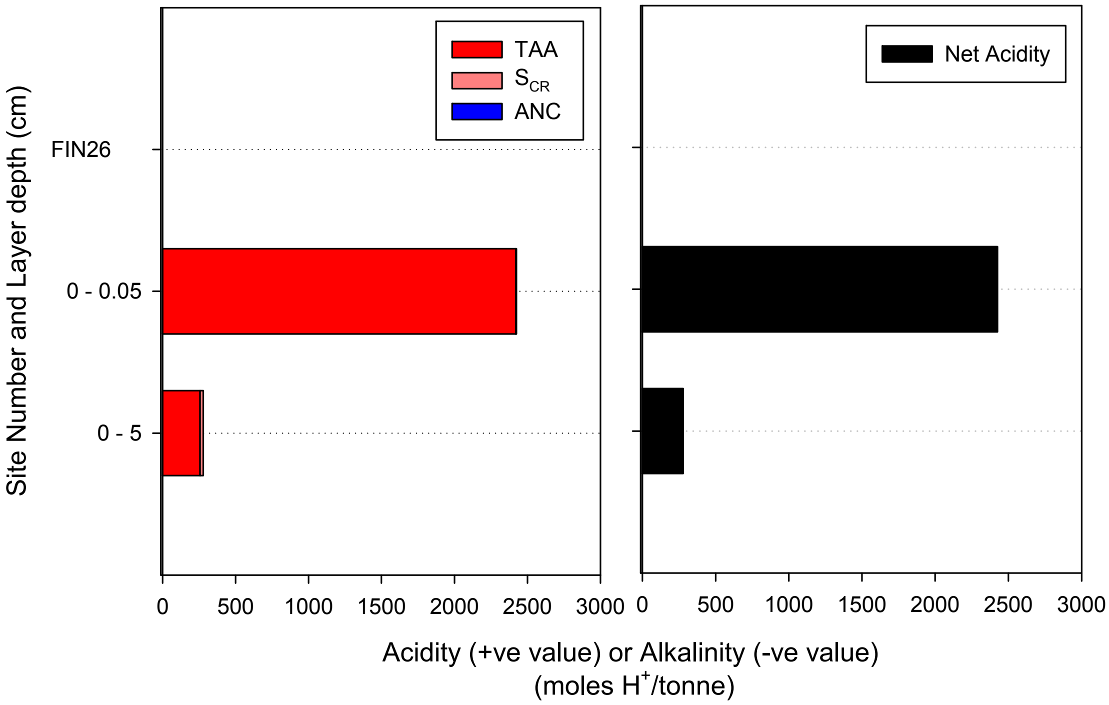


Figure 6-17: Net Acidity (NA) depth profiles for transect FIN26, Wally's Landing. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

7. BLACK SWAMP

Results from the data are provided under the following sub-headings. A summary of the key findings are listed here.

SUMMARY

The soils of Black Swamp are characterised by shallow ponding of surface water and reeds that are on a thick (80 cm) soft sapric hypersulfidic peaty-clay layer.

The pH_w values are all above the critical value of 4.0 indicating that the soils samples are not sulfuric material, due to the waterlogged conditions with the water table above the soil surface.

However, the pH_{FOX} and $pH_{incubation}$ values indicated that the soil samples have the potential to acidify rapidly on exposure to air (oxygen) and moist conditions. These acid sulfate soil materials classify as hypersulfidic material.

The Net Acidity values ranged from 606 to 25 moles H^+/tonne, all soil samples analysed were positive indicating that they either contain existing acidity and / or have the potential to further produce acid as they oxidise.

7.1. Site and Soil Characteristics – Black Swamp

Black Swamp area that is part of the lower Tookayerta Creek had 1 soil profile described and sampled, the site position is shown in Figure 1-1, co-ordinates and site description are presented in Table 3-1, and profile description in Appendix 3. No transects were placed through the area and the one site is regarded as reasonably representative of this part of the swamp area.

The soil was under about 20 cm of water amongst reeds in a swamp area. The soil consisted of 80 cm of firm peat overlying black, soft, peaty clay.

7.2. Acid Generating Potential – Black Swamp

7.2.1. Soil pH testing (pH_W, pH_{FOX} and $pH_{incubation}$)

Soil pH data for 3 soil samples from 1 soil profile site measured in the Black Swamp area are listed in Appendix 4. These values are presented below as pH depth plots (Figure 7-1).

The pH_w values ranged from 4.8 (FIN29 80-100 cm) to 5.6 (FIN29 5-15 cm). All three samples where above the critical pH_w value of 4.0.

Following treatment with peroxide the soil pH dropped significantly and pH_{FOX} values ranged from 1.3 (FIN29 80-100 cm) to 1.9 (FIN29 15-80 cm). All three samples were below the critical pH_{FOX} value of 2.5, which indicates the soil may have the potential to acidify to less than pH 4 on exposure to air (oxygen) under moist conditions.

Chip-tray soil samples were aged and measured for pH at 11 and 20 weeks. The 20 week pH values are presented in Figure 7-1 and the 11 week pH values are listed in Appendix 4. The 20 week $pH_{incubation}$ values ranged from 2.5 (FIN29 80-100 cm) to 4.5 (FIN29 0-15 cm). The two lower samples dropped to below 4.0, indicating a more realistic scenario with regard to what will happen during rewetting of the soils.

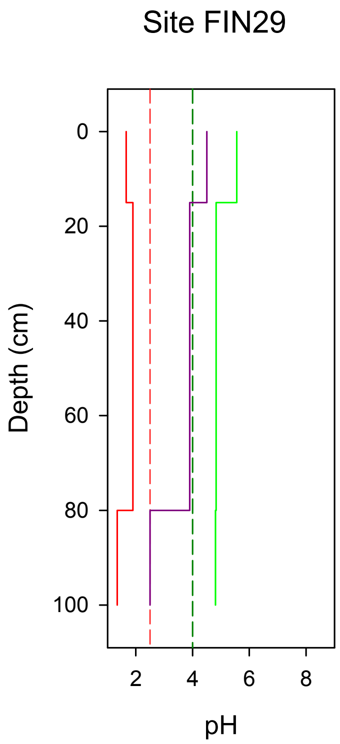


Figure 7-1: Depth profiles of pH for transect FIN29, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after 20 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (black dashed line) and critical pH_{FOX} value of 2.5 (red dashed line).

7.2.2. Sulfur chemistry and acid-base accounting

Acid-base accounting data for three soil samples from one soil profile measured in the Black Swamp area are listed in Appendix 5. These values are presented below as Net Acidity plots and plots showing the components of the Net Acidity (Figure 7-2).

Three samples that had a pH_{KCl} below 6.5, indicating they contain existing acidity as TAA. Where measurements of pH_{KCl} are below 6.5, by definition ANC is considered to be zero.

The Net Acidity values ranged from 805 to 222 moles H^+/tonne, and all three soil samples analysed were positive. This indicates that all (i.e. 100%) of the soil samples either contain existing acidity and / or have the potential to further produce acid as they oxidise.

Water extractable sulfate values are very high with all samples having greater than 100 mg SO_4 /kg of soil.

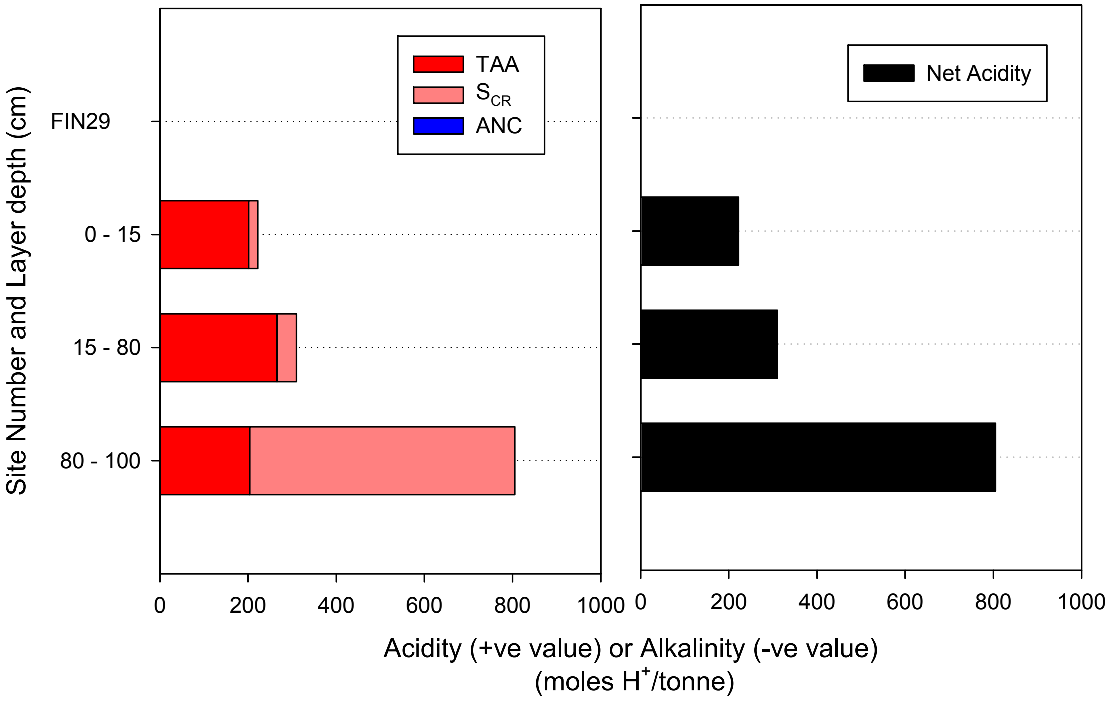


Figure 7-2: Net Acidity (NA) depth profiles for transect FIN29. Showing on the left side the components TAA (red bar), AGP as S_{CR} (pink bar), and ANC (blue bar).

8. HAZARD ASSESSMENT

This study aimed to verify the presence (or absence) of acid sulfate soil material and if present determine their level as a hazard.

It is only relatively recently that the extent of inland acid sulfate soils has been realised (Fitzpatrick *et al*. 2008a,b,c; Shand *et al*. 2008a). The nature, type and distribution of inland acid sulfate soils, the environments in which they occur (e.g. wetlands, river and stream channels), and the potential impacts on surrounding ecosystems make them more complex than their coastal equivalents, and a detailed and robust strategy has yet to be developed. Nevertheless, the potential problems associated with inland acid sulfate soils have recently been studied in some detail (Fitzpatrick *et al*. 2008a,b,c; Shand *et al*. 2008a; Simpson *et al*. 2008) and form the basis of this hazard assessment.

This study has used robust and tested coastal and inland acid sulfate soil assessment methodologies (e.g. peroxide testing, acid-base accounting, water soluble sulfate, soil incubation/ageing and surface and ground water quality measurements) to characterise the acid sulfate soil material types identified in the Finniss River, Currency Creek, Goolwa Channel and Black Swamp areas.

Two methods of hazard assessment are used and these are discussed below.

8.1. Acid Hazard Classification Based on Soil Net Acidity and Lime Treatment Category

The acid hazard classification assessment for acid sulfate soil materials is conducted according to a well recognised and set criteria established for preparing coastal acid sulfate soil management plans (Dear *et al.* 2002). The acid hazard class assigned to the soil layers range from Low to Very High and these ratings relate to the amount of lime required to neutralise the net acidity (Lime Treatment Category) in order to maintain a soil pH above 5.5. The site acid hazard classification is assigned by determining the soil layer within each soil profile requiring the highest lime treatment (to neutralise Net Acidity) and with a total thickness of at least 15 cm.

The acid hazard class is based on a simplified version of Table 2 from Dear *et al*. (2002) which estimates lime treatment classes. This simplified interpretation for use in this study is presented in Table 8-1, it is modified here in three ways:

1) the 500 tonne level of disturbed material is used. This approximates to about 20m x 20m x 1m of disturbed material,
2) existing plus potential net acidity is expressed in mol H^+/t instead of converting these values to %S_{CR}, and
3) a ‘No treatment’ class (N) has been added and approximate ‘Low treatment’ (L) class added for the 500 t disturbed acid sulfate soil level set at the S_{CR} analysis level of 0.01%.

Users are referred to Table 2 in Dear *et al*. (2002) for details relating to lime use and quality. It should be noted that the lime figures provided show a relative difference between soil samples as a measure of soil net acidity, they are not necessarily a recommended lime rate for management purposes, as this requires input of other information such as the chemistry of the surface/receiving waters to be considered.

The assignment of the acid hazard class based on the lime treatment category for each of the soil layers analysed is listed in Appendix 6.

Each of the soil layers in a profile has then been assessed to determine the overall classification for the site; this is presented in Table 8-2 along with an assessment of the acid sulfate soil material that characterises the greatest hazard at the site.

The summary of sites in each class is shown in Table 8-3. All (94%) but 2 sites have sufficient net acidity that, if disturbed, would require treatment. More than 91% of the sites assessed have a high, very high, or extra high hazard classification indicating a significant potential acid hazard.

Table 8-1. Table for estimating acid hazard classification based on a modification of Table 2 from Dear *et al*. 2002.

	Soil Analysis - Net existing plus potential acidity					
Net acidity (mol H^+/t)	≤ 0	>0 to ≤6	>6 to ≤37	>37 to ≤250	>250 to ≤940	>940
Equivalent S_{CR} (%)	≤0	>0 to ≤0.01	>0.01 to ≤0.06	>0.06 to ≤0.4	>0.4 to ≤1.5	>1.5
Lime treatment level (t/500t soil)	nil	>0 to ≤0.3	>0.3 to ≤1	>1 to ≤5	>5 to ≥25	>25
Acid Hazard class - Code	**N**	**L**	**M**	**H**	**VH**	**XH**
Acid Hazard Class	No hazard,	Low hazard,	Medium hazard,	High hazard,	Very High hazard,	Extra High hazard,
Definition – Lime Treatment Category	No treatment	Low treatment (< 0.3 t)	Medium treatment (> 0.3 to 1 t)	High treatment (> 1 to 5 t)	Very High treatment (> 5 to 25 t)	Extra high treatment

Table 8-2. Acid hazard assessment as determined by the lime treatment category for each site.

Site Number	**ASS Soil Code No.**	**Soil Material Type Category**	**Acid Hazard Class* Lime Treatment Category**
CUR 11		hypersulfidic	VH
CUR 12		sulfuric	H
CUR 13		sulfuric	H
CUR 14		hyposulfidic (S_{CR}<0.10%)	N
CUR 15		sulfuric	XH
CUR 16		hyposulfidic (S_{CR}<0.10%)	L
CUR 17		sulfuric	VH
CUR 18		sulfuric	XH
CUR 19		sulfuric	XH
CUR 20		hypersulfidic	VH
CUR 21		Sulfuric	XH
CUR 22		n.d.	n.d.
CUR 23		sulfuric	VH
CUR 24		n.d.	n.d.
CUR 25		sulfuric	VH
CUR 26		hypersulfidic	H
CUR 27		sulfuric	H
CUR 28		n.d.	n.d.
FIN 20		sulfuric	VH
FIN 21		sulfuric	VH
FIN 22		n.d.	n.d.

Site Number	ASS Soil Code No.	Soil Material Type Category	Acid Hazard Class* Lime Treatment Category
FIN 23		sulfuric	VH
FIN 24		sulfuric	VH
FIN 25		hypersulfidic	VH
FIN 26		sulfuric	VH
FIN x		n.d.	n.d.
FIN 27		hypersulfidic	VH
FIN 28		sulfuric	XH
FIN 29		hypersulfidic	VH
FIN 30		sulfuric	VH
FIN 31		sulfuric	H
FIN 32		hypersulfidic	H
FIN 33		hypersulfidic	VH
FIN 34		n.d.	n.d.
FIN 35		hypersulfidic	H
FIN 36		hypersulfidic	VH
FIN 37		n.d.	n.d.
FIN 38		hypersulfidic	VH
FIN 39		hypersulfidic	N

*Acid Hazard Class and Lime Treatment Category codes used in the table are defined as follows:

N = No hazard, No treatment
L = Low hazard, Low treatment (< 0.3 t)
M = Medium hazard, Medium treatment (> 0.3 to 1 t)
H = High hazard, High treatment (> 1 to 5 t)
VH = Very High hazard, Very High treatment (> 5 to 25 t)
XH = Extra High hazard, Extra high treatment
n.d. = Not determined, site sampled only for water or mineralogy, no soil collected

Table 8-3. Summary number of sites in each acid hazard classes based on the lime treatment category

Acid Hazard Class		Number of Sites	Percentage of sites
N	No	2	6
L	Low	1	3
M	Medium	0	0
H	High	7	22
VH	Very high	17	53
XH	Extra high	5	16
Sub Total of assigned Sites		32	100
n.d.	No data	7	
Grand Total		39	

8.2. Acidification, Metal Mobilisation, and De-Oxygenation Hazards Determined by Soil Material Categorisation

The methodologies used (peroxide testing, incubation (ageing), acid-base accounting, chromium reducible sulfur and water soluble sulfate) were combined to determine the type of acid sulfate soil material as described in Section 1.4 for each of the layers in the soil profile. Then for each soil profile a determination was made by considering the soil layer categories, to select the acid sulfate soil material type that best described the hazard at the site. The acid sulfate soil material determined for each soil layer analysed and the overall site assessment is listed in Appendix 6. Presented in Table 8-2 is the assessment of the acid sulfate soil material that characterises the greatest hazard at the site and the summary of the number of sites that occur in each area is presented in Table 8-5. All of the sites also meet the criteria of potentially monosulfidic.

The hazard type and condition of these soil materials for the specific risks of acidification, metal mobilisation and deoxygenation can be determined by relating with the relationships identified in Table 8-4.

Each acid sulfate soil material type identified may present or has the potential to present a number of environmental hazards, specifically:

- **acidification** (of soil, groundwater and surface waters),
- **metal mobilisation** (from acid sulfate soil material to groundwater and surface water), and
- **deoxygenation** of surface waters.

The hydrogeochemical processes that are responsible for these hazards are inherently linked, in that both acidification and deoxygenation are likely to cause the mobilisation of metals. These hazards may present a **'current'** risk to environmental receptors - where the hazard has been measured or observed, **or** present a **'potential'** risk to environmental receptors - where laboratory analyses of soil properties indicates that a hazard is likely to eventuate if environmental conditions are changed. The general relationship between the acid sulfate soil material types and the hazard condition is presented in Table 8-4.

Table 8-4. General relationships between acid sulfate soil material types and hazard condition.

Type of Acid Sulfate Soil Material	Hazard Type and Condition		
	Acidification	**Metal Mobilisation**	**Deoxygenation**
Sulfuric	current	current	none
Hypersulfidic	potential	potential	none
Hyposulfidic (S_{CR} ≥ 0.10%)	potential	potential	none
Monosulfidic (observed)	potential	current	current
Monosulfidic (potential)	potential	potential	potential
Hyposulfidic (S_{CR} < 0.10%)	potential	potential	none
Other acidic (pH_W &/or $pH_{incubation}$) 4 to 5.5 soil materials	current or potential	current or potential	none
Other soil materials	none	none	none

Seven sites are marked as 'not assessed' because these sites were sampled either for water or mineralogy and soil samples where not collected for laboratory analysis. A review of the field notes indicates that it is highly likely that 5 of these sites would be categorised as 'sulfuric' and 2 as 'hypersulfidic', thus increasing the overall proportion of sulfuric sites.

The results show that over half of the sites are considered as sulfuric, with the remainder essentially being hypersulfidic. The 2 sites identified as hyposulfidic occurred in sand higher up in the landscape and the other under water. The data indicates that these sites are marginal to hypersulfidic.

The widespread spatial distribution of sites means that the study area has a current acidification and metal mobilisation risk (sulfuric material) and if not then there is a high potential of acidification and metal mobilisation (hypersulfidic material) that could become sulfuric. As outlined:

- Sulfuric soil materials pose a *current* acidification and metal mobilisation hazard to local groundwater and surface waters.
- Hypersulfidic materials pose a potential acidification risk to soils, and subsequently to groundwater and surface waters, if the hypersulfidic materials are dried out.
- Hyposulfidic materials also pose an acidification risk to soils, but are less likely to acidify when exposed to air due to higher self neutralising capacities. Hyposulfidic materials ($S_{CR} \geq 0.10\%$) generally pose a higher acidification risk than Hyposulfidic ($S_{CR} < 0.10\%$) due to them containing a higher iron sulfide content, and because the measured acid neutralising capacity (carbonate content) of the soil is sometimes overestimated, when not all carbonate is able to react under field conditions.
- Monosulfidic materials pose a 'current' deoxygenation hazard to small (surrounding) surface water bodies. All soil profiles contained a water extractable sulfate content of >100 mg /L and are therefore considered to have the potential to form monosulfidic material if the soils are re-flooded.

Table 8-5. Acid sulfate soil material types counted by site occurrence.

Acid Sulfate Soil Material Type	**Number of Sites and Percentage of Sites Accessed by Area**				
	Finniss River	**Currency Creek**	**Goolwa Channel**	**Black Swamp**	**Total**
Sulfuric	8 (50%)	4 (67%)	6 (67%)		18 (56%)
Hypersulfidic	8 (50%)	2 (33%)	1 (11%)	1 (100%)	12 (38%)
Hyposulfidic ($S_{CR} \geq$ 0.10%)					0
Hyposulfidic ($S_{CR} <$ 0.10%)			2 (22%)		2 (6%)
Other acidic pH_w &/or $pH_{incubation}$ 4 to 5.5 soil materials					0
Other soil materials					0
Subtotal - Sites Assessed	20	6	12	1	32
Not determined (these sites were sampled for water or mineralogy, the soil was not sampled for analysis)	4		3		7
Monosulfidic (observed)					0
Monosulfidic (potential)	16	6	9	1	32

9. SPATIAL DISTRIBUTION

During 18 to 26 November 2008, 131 soil layer samples in the Currency Creek, Finniss River, Tookayerta Creek and Black Swamp region adjacent to Lake Alexandrina (Figure 1-1) were assessed and sampled. These samples were taken from 39 geographically well-distributed and regionally representative sub-aqueous, waterlogged and drained soil profiles. Investigations of 12 representative transects (or soil hydro-toposequences) - mostly across dry wetlands, dry river beds, dry lake beds and in-river-channels (subaqueous and waterlogged soils) - have shown that the decrease in water levels in the area since the baseline study was conducted by Fitzpatrick *et al*. (2008b) has resulted in exposure of significant new areal extents of subaqueous and waterlogged soils, and formed large areas of acid sulfate soil with sulfuric materials (approximately 2000 ha in November 2008). The map shown in Figure 9-1 is the projected extent of sulfuric and sulfidic materials at –1.0 m AHD, which closely approximates the extent of these materials identified in this study in late December 2008 when the water level was –0.7 m AHD.

Figure 9-1 presents maps depicting the occurrences of various acid sulfate soil subtypes for: (a) water levels at –0.5 m AHD (February, 2008) when the soils were originally mapped; (b) previously predicted occurrence at –1.0 m AHD, which closely relates to present levels and confirmed in this study from field work along 12 transects in late November 2008; and (c) predicted occurrence for a future scenario of –1.5 AHD (modified from Fitzpatrick *et al*. 2008b).

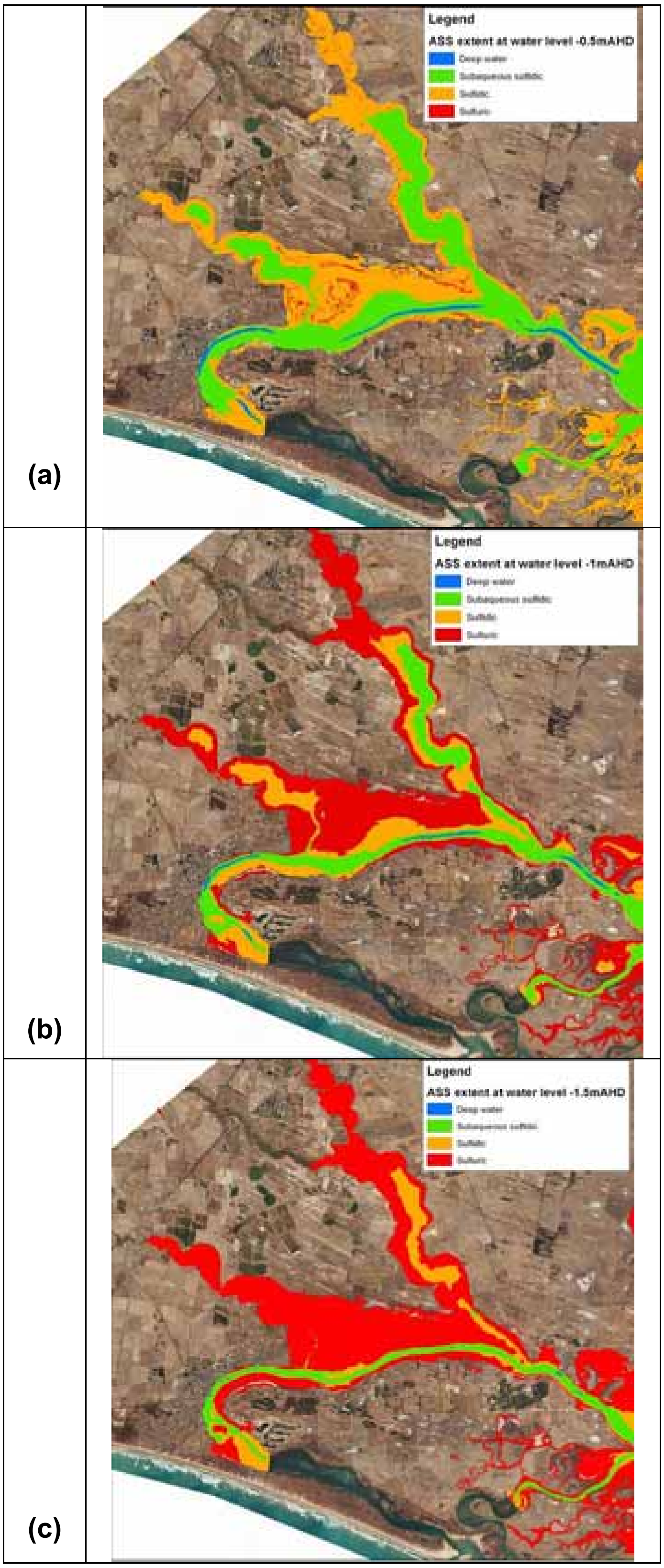


Figure 9-1 Maps depicting the occurrences of various acid sulfate soil subtypes for: (a) water levels at –0.5 m AHD (February, 2008) when the soils were originally mapped; (b) previously predicted occurrence at –1.0 m AHD, which closely relates to present levels and confirmed in this study from field work along 12 transects in late November 2008; and (c) predicted occurrence for a future scenario of –1.5 AHD (modified from Fitzpatrick *et al*. 2008b).

10. PREDICTIVE ACID SULFATE SOIL MODELS: TIME DEVELOPMENT SEQUENCES ILLUSTRATING FORMATION AND TRANSFORMATION PROCESSES

Background

The whole River Murray system is a good example of a system which is not only highly stressed but has been highly managed for decades. The construction of locks, weirs and barrages in the early part of the 20th Century to contain water flow has resulted in extensive agricultural development. However, the permanent inundation of the river, wetland and lake systems has had a significant impact on the formation of soils in these ecosystems because of loss of natural wetting-drying cycles so important to biodiversity and wetland functioning. Sulfide materials have formed and accumulated naturally, however this change has promoted the build-up of sulfide minerals (mostly iron sulfide) and sulfidic materials in these subaqueous soils for over 50 years.

However, prolonged extreme drought conditions in large parts of the system (e.g. Finniss River at Wally's Landing, see Figure 6-5) has caused water levels to recede in the Finniss River and adjacent wetland systems (including the freshwater Lower Lakes: Albert and Alexandrina), which have begun to dry, uncovering extensive areas of sulfidic material in the subaqueous soils (Fitzpatrick *et al*. 2008a,c,d). These soils are much more abundant in these riverine and lacustrine environments than previously recognised. Following drainage, hypersulfidic material in the anaerobic soils has oxidised and transformed to sulfuric material (pH <4), with consequent water quality, ecological and public health issues from metal/metalloid mobilization, de-oxygenation, noxious gas release and wind erosion.

Predictive conceptual models illustrating sequential changes in the formation and transformation of hypersulfidic and sulfuric materials at different water levels for two transects across the Finniss River and adjacent wetlands

Fitzpatrick *et al*. (2008c,d) have identified a generalized conceptual model comprising four sequential phases (or classes of ASS) that form depending on drainage conditions (See Figure 1-2). Soils range from deep submerged sediments (> 2.5 m) to subaqueous soils (< 2.5m) to waterlogged/saturated (all anaerobic) to unsaturated (aerobic) drained soils (e.g. Wally's Landing, see Figure 6-5). Based on field investigations and historical/palaeo-pedological knowledge of the Finniss River, we have constructed a series of eleven conceptual models that illustrate how various ASS materials in subaqueous, waterlogged (saturated) and dried conditions have sequentially changed, and have also recently changed because of rewetting from recent winter rainfall events.

Finniss River transect at Wally's Landing

To illustrate sequential changes in ASS materials at different water levels caused by drying (drought triggered) and rewetting (recent winter rains), we have constructed a series of conceptual models consisting of seven cross-sections across the Finniss River at Wally's Landing (A – A') (Figure 10-1; Figure 10-2).

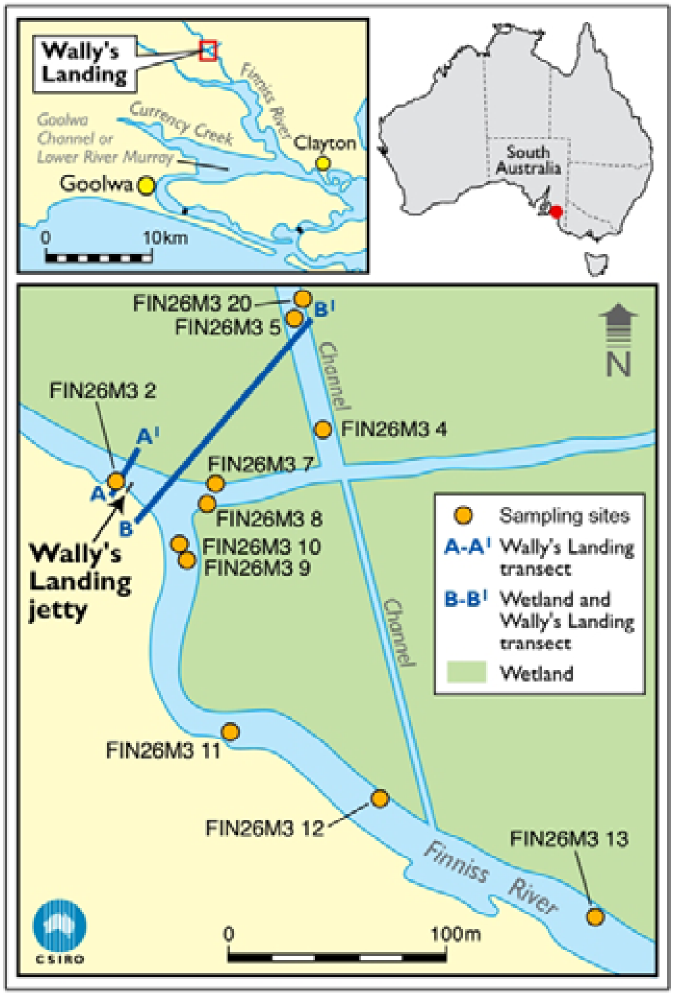


Figure 10-1: Locality map of upper Finniss River area showing localities of two transects or cross sections (A–A' at Wally's Landing jetties across the Finniss River and B – B' across the Finniss River and adjacent wetland/channel) and for water and soil profile monitoring sites during rewetting from winter rainfall events.

(i) Before the 1880s (5,500 BCE to 1880s), the Finniss River cycled between natural wetting and flushing, and partial drying conditions in response to seasonal (i.e. winter/summer) and climatic (e.g. drought/wet) cycles occurring in the upper MDB (Figure 10-2).

During wetter periods, the Finniss River underwent regular wetting and flushing cycles (Figure 10-2 - upper panel). Waters in the Finniss River were transferred via channels, overland flow, and by infiltration. The river accumulated hypersulfidic materials from sulfate contained in surface waters and groundwaters. However, during dry periods such as droughts (Figure 10-2 - lower panel) when river flows were lower, the Finniss River and adjacent wetlands partially dried, causing oxidation of sulfidic materials, especially on the dry margins. Pyrite in the hypersulfidic material was oxidised with likely formation of sulfuric acid and potentially the formation of sulfuric materials. In wetter times and during floods, the acidic material was submerged in the water column, with dilution/neutralisation of acidity and the reformation of hypersulfidic material. The build-up of hypersulfidic materials in the Finniss River was regularly kept-in-check by oxidation and removal during scouring floods.

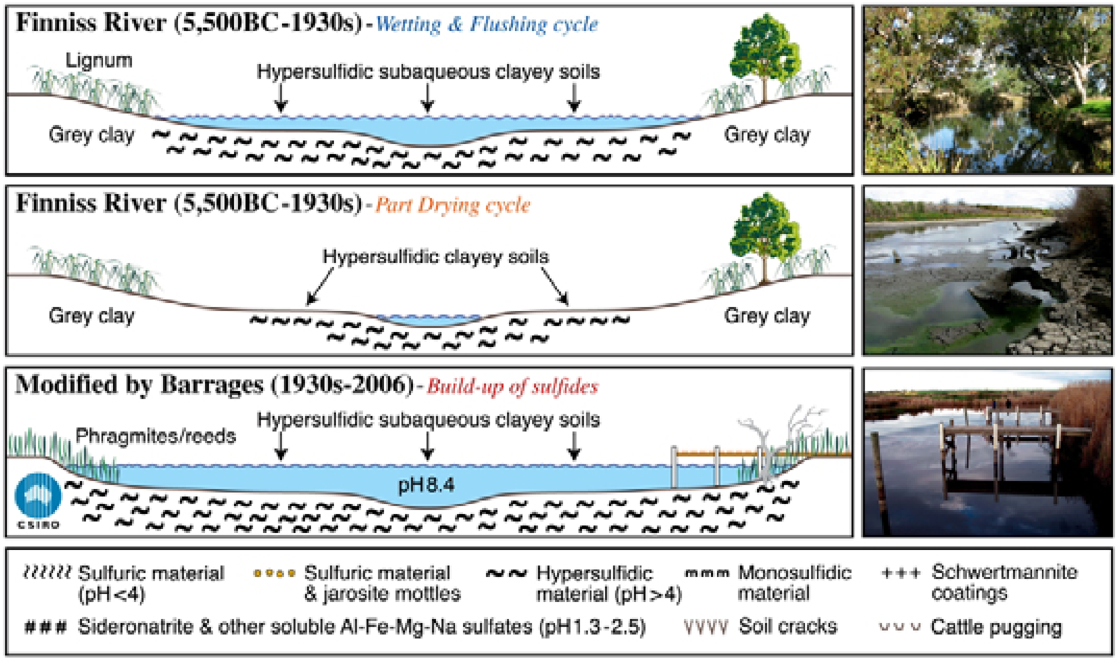


Figure 10-2: Generalised schematic cross section models for Finniss River near Wally's Landing (see Figure 10-1 A – A') illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycle conditions during the time prior to major pre-European development (5,000 BCE to 1880s).

(ii) **During the 1930s**, when Lake Alexandrina and Finniss River were first managed using locks and barrages, to 2006 (Figure 10-2).

During the 1930s to 2006 period, the Finniss River was managed using locks and barrages. The installation of locks and barrages allowed considerable build-up of hypersulfidic and monosulfidic material in the lower lakes and tributaries (subaqueous hypersulfidic materials) due to: (i) the evaporative concentration of sulfate containing nutrient/salt loads in stable pool levels and groundwater sources, (ii) the lack of scouring and seasonal flooding. Ultra-fine monosulfidic material accumulated in low-flow backwaters and along the vegetated edges of the wetland.

(iii) **During the 2006 to November 2008** period when partial drying of the river and adjacent wetlands took place (Figure 10-3).

During the 2006 to November 2008 period, partial drying of the river and adjacent wetlands took place (Figure 10-3), due to drought conditions, and the river and lake levels continued to decrease. During this period, subaqueous ASS transformed to waterlogged ASS (i.e. ASS that are wet or saturated long enough to produce periodically anaerobic conditions, thereby influencing the growth of plants: e.g. hydric soils with hypersulfidic material) and eventually to dried ASS.

(iv) **During November 2008 to February 2009** period when extreme drying of most of the river and adjacent wetlands took place (Figure 10-3).

During the November 2008 to February 2009 period, complete drying (unprecedented in recent history) of Lake Alexandrina and adjacent whole wetlands took place (Figure 10-3) because of the extreme drought conditions from 2006 to February 2009, when the river and lake levels continued to lower. Most wetlands adjacent to Lake Alexandrina effectively became hydraulically disconnected from the lake. This resulted in the formation of sulfuric material (pH less than 4 to depths up to 50cm). Under such low pH conditions, acid dissolution of the layer silicate soil minerals is likely to have caused the release of Fe, Al, Mg, Si (and others) (Figure 10-3). These conditions have also permitted deepening of desiccation cracks (> 50cm), especially in areas that are organic-rich (>10 % organic carbon) and clayey (>35 % clay). The continued drying of the Finniss River and the adjacent wetlands has caused further desiccation, and the precipitation of sulfate-rich salt efflorescences in desiccation cracks and on the sandy edges on the river (Figure 10-3). Areas with monosulfidic materials continued to dry out, also causing desiccation cracks to develop in the fine textured material.

(v) During May 2009 period when rewetting from winter rains took place (Figure 10-3)

During May 2009 rewetting of the river and adjacent wetlands (cracks and cattle pugging areas have filled with water) causing sulfate-rich salt efflorescences to dissolve and wash into cracks and cattle pugs (pH 2.8 to 4) and the river to have a pH of 7.1.

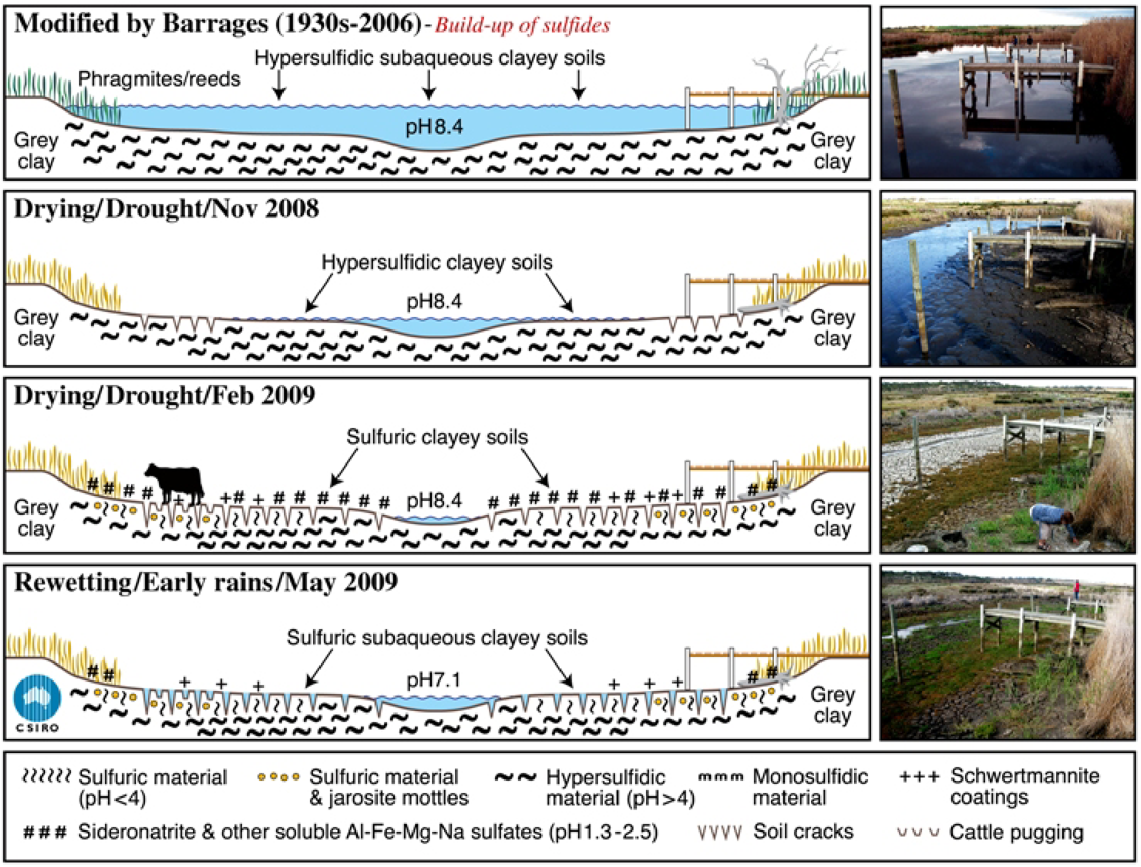


Figure 10-3: Generalised schematic cross section models for the Finniss River at Wally's Landing illustrating modification of water flows by barrage installations causing the build up of sulfides under continuous subaqueous ASS conditions from 1930s-2006 followed by progressive drying (middle two panels), and finally a rewetting phase in May 2009 (lower panel) resulting in acidic waters in the cracks and cattle pugs, and in running waters in adjacent wetlands.

Wetland-Finniss River transect

Finally, to illustrate sequential changes in ASS materials at different water levels caused by drying (drought triggered) and rewetting (recent winter rains) in a wetland adjacent to the Finniss river, we have constructed a series of conceptual models consisting of 4 cross-sections across the Finniss River at Wally's Landing (B – B') (Figure 10-1; Figure 10-4).

(i) Stable pool levels for period from the 1930's to 2006, when Lake Alexandrina and Finniss River were first managed using barrages and locks, to 2006 (Figure 10-4), stream water pH 8.4.

As indicated above during the 1930s to 2006 period, the Finniss River and adjacent wetlands were managed using locks and barrages to maintain stable pool levels of freshwater. The installation of locks and barrages allowed considerable build-up of hypersulfidic and monosulfidic material in the wetlands and Finniss River (subaqueous hypersulfidic materials) due to: (i) the evaporative concentration of sulfate containing nutrient/salt loads in stable pool levels and groundwater sources, (ii) the lack of scouring and seasonal flooding. Ultra-fine monosulfidic material accumulated in low-flow backwaters and along the vegetated edges of the wetland.

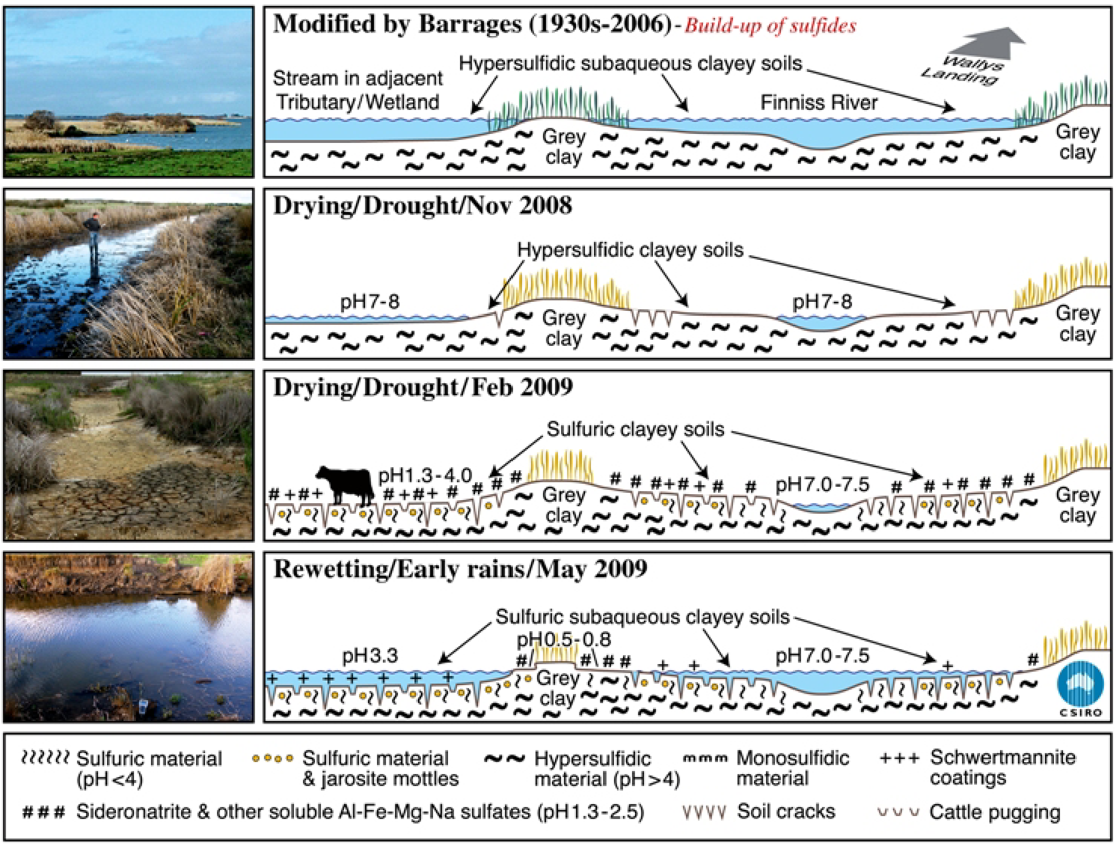


Figure 10-4: Generalised schematic cross section models for an adjacent river wetland (see B – B' transect in Figure 10-1) across the Finniss River and adjacent wetland illustrating modification of water flows and progressive drying (middle upper panels), and finally a rewetting phase in May 2009 (lower panel) resulting in acidic pools and running water (pH 3.3. to 4) in the cracks and cattle pugs (pH 0.5 to 0.8).

(ii) Partial drying period from 2006 to November 2008 when extreme drying of most of the river and adjacent wetlands took place (Figure 10-4), stream water pH 7 to 8.

From 2006 to November 2008 partial drying (unprecedented in recent history) of the Finniss River and adjacent wetlands took place (Figure 10-4 – panel 2) because of the extreme drought conditions, when the river and lake levels continued to lower.

(iii) Extreme drying period from November 2008 to February 2009 when extreme drying caused the wetland and more elevated banks along the Finniss river to be completely dry (Figure 10-4 – panel 3), soil pH 1.3 to 4.

All wetlands adjacent to the Finniss River effectively became hydraulically disconnected from the Finniss River during this summer period, which experienced extreme heat waves and drought. This resulted in the formation of sulfuric material (pH less than 4) to depths up to 50 to 75 cm. Under such low pH conditions, acid dissolution of the alumino silicate soil minerals are likely to place causing release of Fe, Al, Mg, Si (and others) elements and the subsequent formation of various iron oxyhydroxysulfate minerals (e.g. schwertmannite and sideronatrite) and salt efflorescences (Figure 10-4 panel 3; see Figure 6-5). These conditions have also permitted deepening of desiccation cracks (> 50cm), especially in areas that are organic-rich (>10 % organic carbon) and clayey (>35 % clay). The continued drying of the Finniss River and the adjacent wetlands has caused further desiccation, and the precipitation of sulfate-rich salt efflorescences in desiccation cracks and on the sandy edges on the river (Figure 10-4 panel 3). Areas with monosulfidic materials continued to dry out, also causing desiccation cracks to develop in the fine textured material.

(iv) Rewetting from winter rainfall events commenced in May 2009, partially refilling the Finniss River and adjacent wetlands and streams (Figure 10-4 – panel 4; Appendix 10), soil; stream water pH 3.3; and rewetting soils (pH 0.5 to 0.8)

Winter rainfall conditions have caused the following wetland systems to refill with acidic waters:

- cracks and cattle pugging areas (pH 2.8 to 4) where soluble sulfate-rich salt efflorescences (e.g. epsomite and hexahydrite) and sideronatrite appear to have dissolved and washed into cracks and cattle pugs (pH 2.8 to 4) causing the formation of orange coloured coatings comprising mainly schwertmannite.
- adjacent flowing (10-15 litres per second) streams or channels (see Appendix 10: Figures A10-1 and Figure A10-3) showing the orange coloured iron oxyhydroxysulfate mineral (schwertmannite) precipitating in the water column,
- adjacent flowing wetlands showing soil cracks under water (see Figure A10-4), which comprise sulfuric materials down to a depths exceeding 50 to 75 cm with: (a) thin brownish-orange precipitates comprising schwertmannite that coat the outside of clayey peds and cracks (0 to 20 cm), (b) sandy gravel layer at 20 to 25 cm with pH 3.4 (Figure A10-6) and (c) very sticky dark grey heavy clay with prominent slickensides and straw coloured yellowish coatings of natrojarosite at 25 to 50 cm (Figure A10-7). The sandy banks adjacent to the streams and along the Finniss River (see Appendix 10: Figures A10-1, A10-2, and Figure A10-3) comprise sulfuric material with extremely low pH levels ranging from pH 0.5 to 0.8 (see Figure 10-4 – panel 4; Figure A10-2).
- Finniss River (Figure 10-4 – panel 4 indicating a pH of 7 – 7.5).

11. CONCLUSIONS

Important conclusions identified from assessment of the data include the following:

- The data indicates that the entire study area is at risk of acidification. More than half of the sites investigated contained sulfuric soil material. The remainder of sites had significant potential for acidification of soils with sulfidic materials but the risk of this occurring is low to moderate provided they are kept under anaerobic conditions.
- Layer distribution of soil materials is better understood and presented as conceptual toposequence models to provide an improved understanding of spatial extent of the acid sulfate soil materials (Figure 4-1, Figure 4-2, Figure 5-1, Figure 6-1, Figure 6-2, Figure 6-3). These figures show that sulfuric material occurs not only on the dry soil surface but also down to 30 cm depth in dry soils, and that this low acid layer is more commonly in clayey soils that have cracks to form columns. Hypersulfidic material occurs throughout either below the sulfuric layer or below surface water or the water table in the soil. The hypersulfidic layer ranges in thickness up to and in some areas more than one metre, and it is often formed in black, soft clay.
- The conceptual toposequence models provide an understanding of the soil distribution that then allowed the earlier predictive maps to be tested and updated with more confidence. Large areas of extremely acidic soils (sulfuric materials: pH < 4.0) were present and confirmed previous predictions (Fitzpatrick *et al*. 2008b) that these areas have a high potential of developing sulfuric materials (i.e. soil pH < pH 4). There is also a high potential of developing more sulfuric materials from existing sulfidic materials, which have not yet oxidised.
- The combined standard methodologies has confirmed these soils either contain sulfuric acid (sulfuric material, pH ≤ 4), or have the potential to oxidise and form sulfuric acid when exposed to air (oxygen) because of high concentrations of sulfide minerals (sulfidic material). The occurrence of both sulfuric and sulfidic materials is believed to be causing acidic soil and waters within the study area.
- The highest risk of acidification is clearly related to the soils and sediments, which already contain sulfuric material, these materials occur in more than half of the sites investigated.
- There is significant potential for acidification of soils with sulfidic materials but the risk of this occurring is low to moderate provided they are kept under anaerobic conditions, these materials occur in the remainder of the sites.
- At several sites, abundant new occurrences of minerals in salt efflorescences and sub-surface horizons were observed. Bright yellowish and orange surface efflorescences and pale yellow mottles in subsoils were present and X-ray diffraction analyses showed that these were sideronatrite, schwertmannite and jarosite/natrojarosite minerals, respectively. The pH values of the bright yellowish surface efflorescences are very acidic (pH < 2) and the orange and pale yellow minerals are acidic (pH < 3 to 4). The presence of all of these minerals indicates high contents of iron sulfides (principally pyrite) in the original materials. It is predicted that much larger quantities of sulfuric acid will be produced in the sulfidic subaqueous soils if the river levels continue to drop significantly and the adjacent wet soils are allowed to dry.
- Metal mobilisation is likely to be most significant in sulfide-containing soils, which have undergone oxidation. Sulfide minerals scavenge trace metals and may therefore release these metals during oxidation.

- The release of nitrate and phosphate from the dried soils was low. The metal release was rapid and dissolved concentrations of Al, Cd, Co, Cu, Cr, Mn, Ni, V and Zn greatly exceeded the Australian water quality guidelines (WQGs) for protection of ecosystem health. For Al, Cd, Co, Cu, Cr, Ni and Zn, the concentrations were often greater than 100×WQGs.
- Greater concentrations of metals were released from Finniss River soils than from Currency Creek soils. There was a weak relationship between the paste-pH of the soils (following collection) with pH of water upon 24 h of resuspension in deionised water. The dissolved metal concentrations, released from the soils to the water, were generally significantly greater when the soil-water mixture had pH <5.
- The tests demonstrated that the rewetting of dried acid-sulfate soils has the potential to release significant quantities of environmentally degrading substances. Although not investigated, the attenuation of dissolved metal concentrations (removal from the dissolved phase) through co-precipitation and adsorption to aluminium and iron oxyhydroxide phases is likely to occur as acidic, metal-rich waters mix with more neutral or alkaline water.
- Some of the waters in soil pits of the dry river-beds and wetlands of Currency Creek (with deep cracks) and Finniss River (sands) had low pH values ranging from 3.4 to 3.9. Some river waters sampled in Currency Creek and Black Swamp contain moderate to low concentrations of alkalinity (<117 mg/L and 31 mg/L respectively as HCO_3). Acid sulfate soil influences on the low alkalinity in Currency Creek are likely when compared to the high alkalinity of Lake Alexandrina water (currently in the range 200 to 250 mg/L). This is because the lower Finniss River and, until recently, Currency Creek are contiguous with Lake Alexandrina via the Goolwa channel and should therefore have had similar alkalinities when water levels were higher. Even with the retreat of the lakes, sporadic movement of lake water up the lower Finniss and Currency channels occurs through wind activity, “seiching”. The alkalinity of Lake Alexandrina thus helps to maintain the alkalinity of the remnant Currency Creek and Finniss River waters, along with local contributions from ground waters and evapo-concentration.

11.1. Recommendations

11.1.1. Monitoring

Monitoring is considered an essential component of acid sulfate soil assessments during the current drought, and will be particularly important during rewetting phases when acidity and metal mobilisation may occur. Monitoring frequency should be assessed based on a number of factors including the degree and extent of risk. This is site and scale dependent. Taking into account the area of the Currency Creek, Finniss River, Goolwa Channel and Black Swamp/ Tookayerta Creek catchments, it is recommended that monitoring be completed at two levels:

1. Detailed monitoring to be completed at selected “reference sites” every two to three months to determine future changes in acid generation, i.e. increase in sulfuric material with depth and increase in spatial extent during the drying or wetting regimes and mobility. This will involve soil sampling and analyses at specified sites along transects, supported by: (i) morphological, (ii) chemical (e.g. Cr-reducible S, retained acidity and acid neutralising capacity), and (iii) mineralogical observations at each reference site.
2. Spatial monitoring on a monthly basis (or when there is a rapid water level change at the sites), as sampled in this study, to assess spatial trends, based

on visual indicators, morphological descriptions and “indicators” of acid generation. Observations should include physical characteristics of soils (e.g. changes in depth of sulfuric materials, depth of cracking, depth to water) and surface mineralogical characteristics (e.g. visually monitor changes in soil that may indicate sulfide oxidation such as brown-orange precipitates or the presence of indicator minerals such as jarosite, schwertmannite or magnesium-rich sulfatic salts).

As well as providing a basis for quantitative estimates of acidity, metal mobility and treatment options, the data from the monitoring exercise can be used to confirm the current acid sulfate soil maps. These maps can be used to illustrate the extent of acidification, to inform decision makers to assist in assessing the risks to local ecosystems.

We recommend that the detailed monitoring program be conducted along at least three transects in both Currency Creek and Finniss River catchments and along at least one transect in the Black Swamp/Tookayerta Creek catchment. However, we recommend that the rapid monitoring be conducted along all 12 transects, which includes all current 39 soil profile sample sites.

Monitoring of the water should be conducted following refilling or inundation to determine any impacts on water quality. This should include alkalinity, pH, SEC, major and trace elements, and nutrients.

11.1.2. Detailed investigations of hot-spots

Undertake a detailed acid sulfate soil survey and investigation of the wetland area north of Wally’s Landing (Figure 1-1), which is a known source of acidic surface water in the Finniss river, to quantify the source, extent and storage of acid production by:

- Conducting a baseline survey to determine the spatial extent of the various subtypes of acid sulfate soil during the current wetting phase and more sampling/monitoring of key identified sites during drying phase until February 2010.
- Making field assessments and undertaking laboratory investigations of the nature and extent of various acid sulfate soil materials (sulfuric, hypersulfidic, hyposulfidic, monosulfidic), acid sulfate soil Subtypes (subaqueous sulfidic soils, sulfidic soils and sulfuric soils) and waters in the tributaries and the wetland area according to the recent field and laboratory methodologies agreed with the Murray-Darling Basin Authority (Fitzpatrick *et al*. 2009b).

Outputs will include:

- Spatial and spatio-temporal maps showing the distribution and changes in acid sulfate soil and measured soil parameters.
- Comprehensive database of all soil and water chemical data.
- Conceptual soil-water-landscape models showing the successive changes in acid sulfate soil materials and measured soil parameters with time.
- Recommendations and provision of underpinning science throughout the project as to whether further remedial options based on the current soil information are required, and when.
- Publish final Report (as a CSIRO Land and Water Science Report) on all findings in relation to envisaged outcomes, especially to determine the source, extent and storage of acid production with relevant maps, diagrams and

detailed appendixes (including all field and laboratory data), including the scientific data necessary to underpin management options, ongoing monitoring and “potential’ short-term mitigation options.

- Publication of scientific findings in scientific literature (post project).

11.1.3. Phase 2 sample selection

At an early stage in this study it was apparent that the soils and sites were either sulfuric or hypersulfidic, a high risk, and would meet the Phase 2 criteria requiring further investigations. Because of the urgent need to obtain data for this area the decision was made to accelerate the Phase 2 sample selection and submit the soils for further analysis. This data, primarily mineralogy and metals analysis has been conducted and reported in this report.

Based on the data and conclusions, all sites investigated during this study meet the criteria to be considered a High Priority (Table 8-5). It is recommended that the remaining Phase 2 tests be undertaken to complete the requirements of the Phase 2 investigations.

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There are 2 versions of the report – one without maps as appendix and one with maps:
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http://www.clw.csiro.au/publications/science/2008/sr12-08_nomaps.pdf

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